VOL. XV. [FEBRUARY, 1893.] NO. 2.

AMERICAN

CHEMICAL JOURNAL.

Contribution from the Laboratory of General Chemistry, University of Michigan.

THE ACTION OF METALS ON NITRIC ACID.

I.—THE REDUCTION OF NITRIC ACID BY COPPER.

BY PAUL C. FREER AND GEO. O. HIGLEY.

Although considerable work has been done on this subject, yet in no case has an attempt been made to isolate all the products of reduction. In 1842 Millon[1] undertook to ascertain the temperature at which pure nitric acid, of varying degrees of concentration, acts upon metals. He found that an acid having a specific gravity of 1.07 does not attack copper at 20° C., but that, upon the addition of a little nitrite of potassium, action immediately begins, and from this he concluded that in the reduction nitrite of copper is first formed, the latter being subsequently decomposed by the nitric acid. This author thereupon suggested that the action of the small quantity of nitrous acid present is comparable to that of a ferment. Millon also discovered that an acid of 1.217 specific gravity began to act upon copper at a temperature as low as —10°, while that of 1.108 attacked the metal only above —2°. From a qualitative study of the products Millon concluded that they depended on: 1. Concentration of acid; 2. temperature; 3. the presence of nitrogen dioxide; and 4. solubility of the products.

At a somewhat later period Gay Lussac[2] disputed Millon's statements, showing that nitric acid, even of a specific gravity of 1.02, attacks copper at a temperature as low as —12°. In some

[1] Ann. chim. phys. [3], **6**, 95.

[2] *Ibid.* [3], **6**, 385.

further experiments this chemist added sulphuric acid of a strength represented by the formula $H_2SO_4 + 9H_2O$ and nitric acid of a specific gravity of 1.07, respectively, to copper in two test-tubes, placed both in a freezing mixture, and thus found that there was no action in either case until nitrogen dioxide (hyponitric acid) was added, whereupon both reacted with equal energy, and therefore Gay Lussac concluded the experiment proved simply that "hyponitric acid" is less stable than nitric acid, and ridiculed Millon's idea of metallic fermentation. His work, like Millon's, was mainly qualitative. It is our own experience that nitric acid, entirely free from lower oxides, of a specific gravity as low as 1.20, reacts with pure copper with the greatest readiness.

In 1871 Bourgoin [1] proved that electrolysis of very dilute nitric acid causes no reduction, hydrogen being evolved at the negative pole. With an acid $HNO_3 + 6.25aq.$, hydrogen is first evolved, this is followed by nitrogen, while, finally, ammonia is produced, and with $HNO_3 + 19aq.$, hydrogen and subsequently nitrogen are obtained; the latter gradually increasing in quantity, attaining a maximum and, in the end, disappearing. No nitrous oxide could be detected. When, in subsequent experiments, a more concentrated solution was employed, no hydrogen was at first evolved; however, a blue coloration, probably due to nitrous acid, was observed around the negative pole; finally, the electrolysis of $HNO_3 + 1\frac{1}{2}aq.$ produced pure nitric oxide for a time and, afterward, a mixture of hydrogen and nitric oxide.

In 1875 Acworth [2] made a series of quantitative experiments with the view of determining the proportions of nitric oxide, nitrous oxide and nitrogen which are formed at different stages of the solution of copper in nitric acid, but no attempt was made to estimate the trioxide and dioxide of nitrogen produced, nor was any investigation of the effect of temperatures, above the ordinary, undertaken. The conclusions of this investigator were:

1. Cold, dilute nitric acid, acting on copper, gives almost pure nitric oxide, the gas containing 90–95 per cent. of that substance, but, with increase of copper nitrate in the solution, the per cent. of nitric oxide diminishes.

2. If a concentrated solution of copper nitrate is added to the acid at the beginning of the experiment, 85 per cent. of the evolved gas is nitrous oxide.

[1] Journ. Pharm. [4], **13**, 266–270. [2] J. Chem. Soc. **18**, 828.

3. Potassium nitrate in solution has little or no effect on the composition of the gas.

4. Ammonium nitrate solution, when added, causes the evolution, chiefly, of nitrous oxide and nitrogen.

5. Zinc, mercury or iron, when treated with nitric acid and ammonium nitrate, chiefly evolve nitrogen.

A little later, Acworth and Armstrong[1] published a paper containing an account of work done by them in the same general direction. This research, however, was more complete, because the action of several metals was investigated, and, in addition, some experiments were made on the effect of temperature, as well as an attempt to account for the whole of the metal employed. This work is, however, open to criticism in several respects:

1. The temperature was not kept constant during the solution of the metal, even in those experiments in which the effect of temperature was to be determined.

2. The liquid was not agitated while the action was in progress, although it is a well-known fact that, when quiet, a distinct layer of the nitrate is formed about the metal, thus changing the conditions of the reaction. Indeed, Acworth himself had previously shown that copper nitrate, when present in the mixture, increases the per cent. of nitrous oxide formed.

3. No attempt was made to determine the amounts of dioxide and trioxide of nitrogen, although these gases are the sole products of the reduction of 1.40 nitric acid by copper. One would think that an evolution of only about two cubic centimeters of gas, by the solution of 350 milligrams of copper, should have led to an investigation of the other substances produced by the reduction; to our minds, the study of the minor products of a reaction, while the major ones are entirely neglected, is of little or no value. Of course, since the relative amount of gaseous products increases as the acid is diluted, this criticism will not apply with equal pertinency to the determinations made with an acid containing a considerable quantity of water. In several other respects, also, Acworth and Armstrong's work seems to us to be very incomplete.

At a date later than that of Acworth and Armstrong's work, Gladstone and Tribe[2] published a very interesting paper on the action of the zinc-copper couple on potassium nitrate, potassium chlorate, etc. The action was shown to be electrolytic, the reduc-

[1] J. Chem. Soc. **32**, 54. [2] *Ibid.* **33**, 139.

tion taking place in the immediate vicinity of the negative metal; the conclusion arrived at being that the hydrogen is probably condensed by the finely divided copper previous to entering into the reaction.

In 1883, Divers[1] did some work in which he showed that metals which are acted upon by nitric acid may be divided into two classes. The metals of the first class (copper, silver, bismuth and mercury), when treated with nitric acid, form neither ammonia nor hydroxylamine, while those of the second class (including tin, magnesium, zinc, cadmium, aluminium and iron) produce ammonia or hydroxylamine, or both. Upon rather slender experimental evidence, Divers has attempted to deduce reasons for a structural formula for nitrous acid and its salts, in which he supposes hydrogen, respectively metal, to be joined to nitrogen; the conclusions which he reaches, however, do not seem to us to follow as a logical result of his work.

A study of the literature of this subject reveals the fact that no investigator has quantitatively determined all of the products of the reduction of nitric acid by metals. Only Acworth and Armstrong have attempted to account for all of the metal dissolved, and even in their results there is a discrepancy of 20 per cent. or more between the equivalent of the products obtained and the weight of metal employed. We, therefore, propose to once more take up the question of the reduction of nitric acid by metals, and, by an improved method, hope to throw additional light upon these complicated reactions.[2]

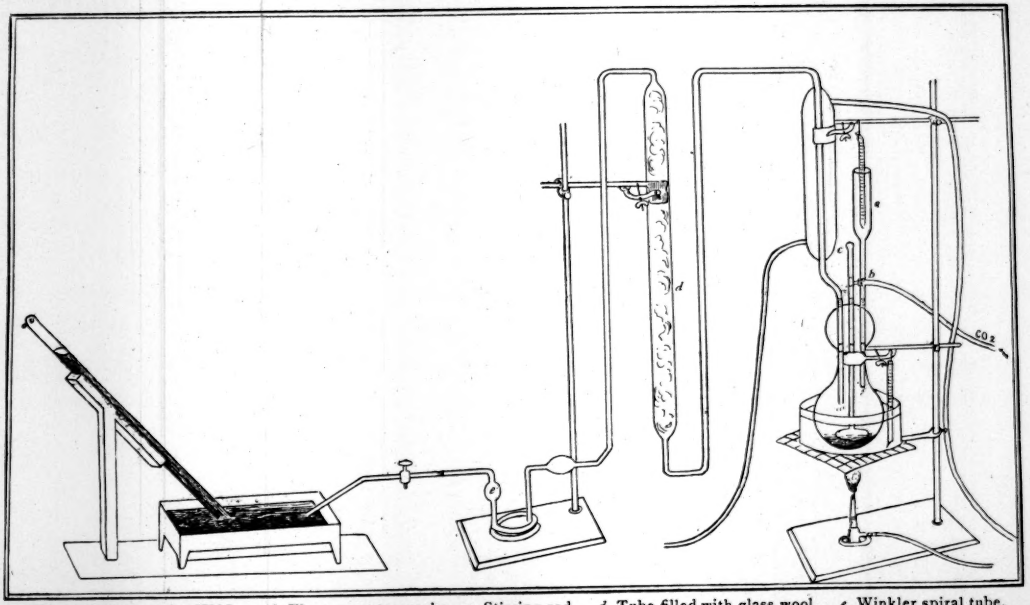
The first series of reactions which we have undertaken to study is that arising from the action of copper on nitric acids of varying degrees of concentration, and, after repeated variations in our method, we have finally constructed a comparatively simple apparatus which gives satisfactory results.

Experimental Part.

Our apparatus consists of a 200-cc. flask, having a ground-glass cap perforated by three tubulures. Into one of these is fitted a dropping-funnel to contain the acid, and having a three-way stop-

[1] J. Chem. Soc. **43**, Trans. 455.

[2] It is obviously too early in the research for us to enter upon a discussion of the bearing which our work has upon the question of nascent action; we intend, however, to critically examine this subject after all of our experimental work has been completed.



a, Dropping funnel for HNO_3. *b*, Three-way stop-cock. *c*, Stirring rod. *d*, Tube filled with glass wool. *e*, Winkler spiral tube.

cock which connects with an apparatus furnishing pure carbon dioxide; the central tubulure is provided with a glass rod carrying a platinum disk for stirring the liquid; the third connects with a Liebig's condenser. The gases pass from this through a long tube filled with glass wool, interposed to remove traces of nitric acid which may be mechanically carried over. A Winkler's spiral tube (containing 35 cc. of pure sulphuric acid, specific gravity 1.84, saturated with nitrous oxide) is attached to absorb nitrogen trioxide and dioxide, the remaining gases passing on to be collected over mercury.

Half a gram of pure copper foil [1] is placed in the flask and then all air expelled from the apparatus by means of a current of carbon dioxide; the flask is at the same time heated to the desired point on a water-bath, after which 15 cubic centimeters of pure nitric acid of the same temperature as the metal is allowed to flow in from the dropping-funnel. During the reaction the liquid is stirred and the temperature carefully regulated until solution is effected; carbon dioxide is now once more admitted, and the flask heated to 100° for one hour, the lower oxides of nitrogen, which are quite soluble in nitric acid (sp. gr. 1.40), being thereby all swept on into the Winkler tube. The contents of the latter are now washed with concentrated sulphuric acid into a graduate, and by addition of a further quantity of that acid the volume is brought up to 100 cubic centimeters, and then the amount of nitrosylsulphuric acid is determined by titration with decinormal permanganate solution. In performing this operation, the best results have been obtained by adding the acid solution to the permanganate, according to the method of Lunge.[2] The total nitrogen is afterward determined as nitric oxide by analysing a portion of the nitrosylsulphuric acid solution over mercury in the nitrometer.[3] From the results obtained in these two operations, the quantity and proportions of nitrogen trioxide and dioxide can be calculated,[4] as is shown below. The nitrous oxide, nitric oxide and nitrogen which have been collected over mercury in the eudiometer tube, are analysed as follows:

The nitric oxide is determined by addition of oxygen with absorption of the excess of the latter by pyrogallol; the nitrous

[1] The foil used in many experiments was very thin and proved itself to be chemically pure. We have also made a series of determinations, using copper wire of 2 mm. diameter, and so discovered that the shape of the copper has no influence on the course of the reaction.

[2] Ber. d. chem. Ges. **10**, 1073. [3] *Ibid.* **11**, 438. [4] *Ibid.* **12**, 357.

oxide is estimated by explosion with hydrogen, and the nitrogen determined by difference.

While we have made a number of determinations with a more dilute acid, when we always obtain considerable nitric oxide, most of the work which has thus far been completed has been done with an acid having a specific gravity of 1.40; with this concentration the reduction-products determined as shown above, have proved to be exclusively trioxide and dioxide. It being possible, however, that some nitric oxide might have been formed in the reaction but subsequently absorbed by the nitrosylsulphuric acid (which, by reason of the reaction between sulphuric acid and nitrogen dioxide, must contain some nitric acid), several determinations were made with the purpose of ascertaining the percentage of absorption of nitric oxide in nitrosylsulphuric acid containing nitric acid.[1] Pure nitric oxide was therefore passed through a Winkler's spiral tube containing 30 cubic centimeters of sulphuric acid to which had been added 0.0895 gram of nitrogen trioxide and 0.0754 gram of nitric acid, the unabsorbed portion of the gas being collected over mercury and the per cent. of loss determined. Two experiments gave the following results:

I. 30.65 cc. lost 19.99 cc.; an absorption of 34.78 per cent.

II. 27.65 cc. lost 18.13 cc.; an absorption of 34.43 per cent.

Obviously, the conditions in these experiments were much more favorable for the absorption of nitric oxide than those which obtain in our ordinary determinations, because in the former there is present from the beginning a considerable mass of nitric and nitrosylsulphuric acids, while in the latter neither is formed in any quantity until the operation has proceeded for some time, the mass present increasing steadily during the reaction. It is to be presumed that, were nitric oxide formed at all, it would pass off among the first reduction-products. It is nevertheless necessary, in order to ascertain whether any nitric oxide is possibly produced during the solution of copper in a great excess of nitric acid having a specific gravity of 1.40, to conduct the experiment with an apparatus which does not necessitate the use of sulphuric acid, and, therefore, we made several determinations with our usual apparatus, substituting, however, for the Winkler tube, three con-

[1] That nitric oxide is somewhat soluble in nitrosylsulphuric acid has already been proven. Ber. d. chem. Ges. **11**, 1643. Veley (Proc. Roy. Soc. **52**, 272) has also recently shown that nitric oxide is quite readily oxidised by means of concentrated nitric acid.

densation-tubes[1] (which together gave a cooling length of about 75 centimeters), kept at a temperature of —20°. By this means, nitrogen trioxide and dioxide were condensed to liquids, and in no case did any appreciable amount of gas (nitric oxide, nitrous oxide and nitrogen) pass on to be collected. The sole products of reduction of nitric acid (sp. gr. 1.40) by copper are, therefore, nitrogen trioxide and dioxide.

Calculations.

The formation of nitrosylsulphuric acid from nitrogen trioxide and dioxide, respectively, may be represented by the following equations:

(1) $2Cu + 6HNO_3 = 2Cu(NO_3)_2 + N_2O_3 + 3H_2O$;

(2) $N_2O_3 + 2H_2SO_4 = 2SO_2\begin{cases} OH \\ NO_2 \end{cases} + H_2O$;[2]

and from the dioxide:

(3) $2Cu + 8HNO_3 = 2Cu(NO_3)_2 + 4NO_2 + 4H_2O$;

(4) $4NO_2 + 2H_2SO_4 = 2SO_2\begin{cases} OH \\ NO_2 \end{cases} + 2HNO_3$.[3]

It follows, then, that the same amount of nitrosylsulphuric acid is produced from the solution of a given weight of copper in nitric acid whether the reduction-product is the trioxide, the dioxide, or a mixture of the two. We see, however (equation 4) that when nitrogen dioxide reacts with sulphuric acid, *one-half of the nitrogen forms nitric acid*, but with the trioxide *nitrosylsulphuric acid alone* is produced; so that when a determination of total nitrogen in the solution is made in the nitrometer, and the result is calculated as trioxide, for the purpose of comparison, the excess in weight of the latter over the weight of trioxide, determined with permanganate, is equivalent to the nitric acid which was present as such in the Winkler tube, and is, therefore, equivalent to one-half the nitrogen dioxide which has reacted upon the sulphuric acid.

Let a represent the weight of N_2O_3 from the nitrometer analysis, and let b represent the weight of N_2O_3 obtained by titration with permanganate; then $2(a-b)$ represents the trioxide

[1] It seems scarcely necessary to mention that the condensation-tubes were fused together so as to avoid rubber connections.

[2] Graham-Otto: Lehrbuch, Vol. I, 657.

[3] Ann. Chem. (Liebig) **123**, 19. *Ibid.* **125**, 293.

equivalent of the dioxide, and $2(a-b)\frac{2058}{1701}$' = weight of dioxide produced; $a-2(a-b)=2b-a$ = weight of trioxide, as such.

If $a=b$, then the reduction-product is trioxide only.

If $a=2b$, then the product is dioxide only.

Results.

Our results, so far as obtained in experiments with acid having a specific gravity of 1.40, are given in the appended table. Experiments 1–3 were made with an apparatus having three short rubber connections, which were coated inside with paraffin, but as, in every case, these connections were slightly attacked by the oxides of nitrogen, there was a consequent loss of reduction-products. We, therefore, so modified our apparatus as to entirely eliminate rubber connections, all parts being fused together except the joint between the glass wool and Winkler tubes, which latter was made by pushing one tube within the other and then sealing the joint with high-melting paraffin. It is for this reason that the first three experiments account for but from 95 to 98 per cent. of the copper, but certainly the last four results, with a variation of only from 100.03 to 100.33 per cent. of the copper, leave nothing to be desired and fully demonstrate the success of our apparatus.

Expt.	Copper. Mgrs.	Acid.		T	Mgrs. N_2O_3. Winkler Tube.		Per cent. of Copper accounted for.	Nitrometer.		Percentage Composition of Gases.	
		Sp. Gr.	Vol. cc.		Calc.	Found.		Corrected Vol. NO.	Equiv. in N_2O_3.	N_2O_3.	NO_2.
1	500	1.40	15	50°	300.33	285.83	95.1	294.8	501.45	11.9	88.1
2	"	"	"	25°	"	290.3	96.6	290.2	493.65	15.1	84.9
3	"	"	"	25°	"	294.6	98.09	298.4	507.5	13.4	86.6
4	"	"	"	0°	"	301.33	100.33	*			
5	"	"	"	0°	"	300.42	100.03	314.	534.1	9.4	90.6
6	"	"	"	10°	"	301.133	100.26	325.0	552.8	7.5	92.5
7	"	"	"	25°	"	300.79	100.15	*			

* No nitrometer determinations in these two experiments were made, the object being only to account for all copper dissolved, as reduction-products.

As regards the ratio between the trioxide and dioxide, however, there is some variation, possibly due in part to varying amounts

[1] One cubic centimeter of NO weighs .001343 gram and is equivalent to .001701 gram N_2O_3 or to .002058 gram NO_2.

of nitric acid which are mechanically carried over by the gases. Control tests, made without the copper, by heating 15 cc. of 1.40 nitric in the flask at 100° for one and a half hours, and then passing a current of carbon dioxide, showed only traces of nitric acid in the Winkler tube, by means of the ferrous sulphate test, and none whatever with the nitrometer; when the trioxide and dioxide are generated, however, they may carry over appreciable amounts of nitric acid, and we therefore purpose adding a much longer tube filled with glass wool, with the hope of entirely eliminating this possible source of error; it is not at all improbable, however, that there may be some variation in the natural course of the reaction. Experiments made since the introduction of this modification in the apparatus have demonstrated that the slight variations are not due to the mechanical addition of nitric acid.

Conclusions.

1. The sole products of reduction of excess of nitric acid, specific gravity 1.40, by copper, are nitrogen trioxide and dioxide; the proportions being about 10 per cent. of the former to 90 per cent. of the latter.

2. The effect of varying temperature upon the proportion of the reduction-products is, apparently, but slight.

Now that an apparatus is completed and satisfactory results have been obtained, we intend to continue the research, to study all the effects of dilution and temperature on the nature and proportion of the reduction-products, extending the work so as to include a number of other metals besides copper, as well as the effects of nitric acid on substances such as cane-sugar starch and arsenic trioxide. We hope by publishing this preliminary article on a portion of the work already accomplished, to reserve this field for ourselves.

Since writing the above, two articles by C. Montemartini[1] have appeared, treating the same subject. The above author has dissolved zinc, iron, cobalt, nickel and cadmium in nitric acid of differing specific gravity, obtaining, in each case, ammonia, nitrous acid, nitrous oxide, nitrogen and nitric oxide, but in each case the reduction-products are considerably in excess of those calculated. Montemartini has also studied the action of nitric acid upon zinc,[2] determining the degree of concentration and temperature at which

[1] Gazetta Chim. **22**, I, 250–265. [2] *Ibid.* 274–343.

a maximum of each reduction-product is produced. The velocity of action between zinc and nitric acid increases regularly with the concentration up to 25 per cent. acid, remains constant between 33 and 42 per cent. and then diminishes regularly, with a minimum at 68 per cent. Montemartini concludes that nitric oxide is always a product of secondary reaction. Our results with copper are certainly more accurate than Montemartini's with zinc, for the fact that the latter investigator always obtains an excess of reduction-products over the calculated quantity still remains to be accounted for; our method seems, therefore, better calculated to lead to trustworthy results than his.

The objection may possibly be advanced that, although we have proven that nitrogen trioxide and dioxide are the sole tangible products of the reduction of concentrated nitric acid by copper, nitric oxide may, nevertheless, be at first formed, to be subsequently oxidised by the excess of nitric acid. In order to ascertain the validity of such a criticism we have performed the following experiment: Five hundred mgr. of copper were placed in the flask of our apparatus and nitric acid was then added, drop by drop, sufficient time for all reaction to cease being allowed between the additions, and this process was continued until all copper was dissolved. By this means an excess of nitric acid was never present, but, nevertheless, no nitric oxide was produced. The conclusion is inevitable, therefore, that the nitric oxide formed when using dilute acid is solely the product of secondary reactions.

MIXED DOUBLE HALIDES OF LEAD AND POTASSIUM.

By Charles H. Herty.

Introduction.

Up to the present, but little work seems to have been done on the subject of mixed double halides. Atkinson[1] describes a salt of antimony, potassium, chlorine and bromine, to which he gives

[1] Jour. Chem. Soc. **43** (1883), 289.

the formula $K_2SbCl_3Br_3.1\frac{1}{2}H_2O$. He also obtained salts corresponding to the formulas $Sb_2Cl_6Br_6K_3.2H_2O$ and $SbCl_3BrK.H_2O$. Pitkin[1] describes the salt $2KBr.PtCl_4$.

Remsen and Richardson,[2] during the course of an investigation of the double halides of tin, made some experiments on compounds of stannous bromide with potassium chloride. Their experiments were limited by a lack of time, and the conclusions drawn necessarily unsatisfactory. Although they describe a salt corresponding closely in composition to the formula $K_2SnCl_3Br_3.2H_2O$, yet from other experiments they were led to believe that another compound which they obtained was "a mixture of the two salts $KSnBr_3.H_2O$ and $KSnCl_3.H_2O$." Recently Wells[3] has published an account of several mixed double halides of caesium and mercury.

As no work has been done on the mixed double halides of lead and potassium, the following investigation was undertaken in the hope of obtaining such compounds as $KPbI_2Br$ ($PbI_2.KBr$), $KPbIBr_2$ ($PbBr_2KI$), etc. As a result of this investigation, it has been shown conclusively that the compounds formed by dissolving lead iodide in an aqueous solution of potassium bromide are mixtures of the salts $KPbI_3$ and $KPbBr_3$, confirming thus the suggestion of Remsen and Richardson.

Method of Analysis.

The method of analysis used in determining the composition of these isomorphous mixtures is based upon the fact that when lead iodide or lead bromide is heated in contact with a solution of sodium carbonate, all of the lead is converted into lead carbonate, while the halogen passes into solution as the sodium salt. The details of the method are as follows:

1. A weighed quantity of the powdered substance, about 1 gram, is heated for two hours at a temperature of 110°. From the loss of weight, water of crystallisation is calculated.

2. The substance, after being thoroughly moistened with water, is transferred to a beaker, and upon it is poured about 25 cc. of water previously boiled in order to expel all carbon dioxide. To this mass is then added a solution of sodium carbonate containing slightly more of the salt than is sufficient to convert all of the lead present into lead carbonate. A gentle heat is then applied for

[1] Chem. News **47**, 118. [2] This Journal **14**, 96. [3] Amer. Jour. of Science **44**, 232.

several hours. The white precipitate which appears on first adding the solution of sodium carbonate is due to the precipitation of the small quantity of lead held in solution by the potassium iodide and potassium bromide present. The solid matter in the beaker soon loses its yellow color and becomes white as the lead is gradually converted into carbonate. The small lumps of lead iodide are broken up by pressing with a glass rod flattened at the end. After the yellow color has disappeared, the heating is continued for one-half hour, in order to insure the conversion of all lead into the carbonate. After cooling, the liquid is filtered off by means of a filter-pump, and the lead carbonate is thoroughly washed with boiled water. Dilute nitric acid is then slowly added to the lead carbonate on the filter, and the lead nitrate washed through the filter, and the lead estimated by precipitation as sulphate.

3. The filtrate from the lead carbonate is heated to boiling and acidified with dilute nitric acid. If the solution now has a yellow tint, the color is removed by adding a few drops of sulphurous acid. Silver nitrate solution is then added in slight excess. After standing twenty-four hours the solution is filtered off, and the precipitate of silver iodide and silver bromide is dried and weighed. The silver salts are then fused in a current of chlorine until a constant weight is attained, and the bromine and iodine estimated in the usual way.

4. In the filtrate from the silver iodide and silver bromide the excess of silver is removed by precipitating with dilute hydrochloric acid and filtering after standing twenty-four hours. This last filtrate is then evaporated to dryness, the dry residue moistened with concentrated hydrochloric acid to insure complete conversion into chlorides of sodium and potassium, and heated again until the mass is thoroughly dry. In the residue the potassium is then determined in the usual manner by conversion into potassium chlorplatinate.

If to a solution of lead iodide or bromide in potassium iodide or bromide sodium carbonate solution be added, all lead is precipitated quantitatively as lead carbonate. This fact furnishes a means for determining the composition of the mother-liquors from which the various compounds described below crystallise. The details of the method are as follows:

1. A portion of the solution, about 5 cc., is drawn off into a weighed porcelain crucible, and the weight of the whole is quickly

determined. The solution is then evaporated to dryness, and the crucible heated for several hours at a temperature of 110°. From the loss in weight, water is calculated.

2. About 5 cc. of water is then added to the residue in the crucible, and heat applied until all dissolves. Sodium carbonate solution is then added until all lead has been precipitated. The contents of the crucible are now washed into a beaker, diluted with water and allowed to settle. The clear solution is filtered off from the lead carbonate. The lead is then determined as sulphate in the manner described above.

3. The filtrate from the lead carbonate is made up to a volume of 500 cc., and in 100 cc. of this solution, iodine, bromine and potassium are determined as described above.

Experimental Part.

Preliminary Experiments.—For the preparation of mixed double salts, the first method which suggested itself was that based upon the solution of lead halides in water-solutions of the alkaline halides. Accordingly, preliminary experiments were made in order to determine what combination of halides furnished the best means for studying the problem. Three portions of a cold saturated solution of potassium iodide were heated almost to boiling; to one was added lead bromide, to another lead chloride, and to another lead fluoride. The lead salts dissolved in each case, and, on cooling, yellowish needles crystallised from each solution in large quantities. During crystallisation a great deal of the water present was taken up as water of crystallisation. This caused so great a concentration of the solution that cube-shaped crystals of potassium iodide crystallised along with the yellow needles. No definite idea of the composition of the yellow needles could therefore be obtained. The compound obtained by solution of lead bromide in potassium iodide seemed to be least contaminated by free alkaline halide, and also to have the most perfect crystalline form, and it was therefore decided to confine attention to the preparation of potassium bromiodoplumbites.

Solution of lead bromide in potassium iodide.—A solution of potassium iodide was prepared, of such a strength that 50 cc. of the solution contained 50.8214 grams of potassium iodide. One portion of this solution, 50 cc., was heated to boiling, and 20 grams of lead bromide added. The white lead bromide became yellow as

soon as it came into contact with the potassium iodide solution. All dissolved except a very slight white residue. The solution was then filtered from this residue through a hot funnel into a hot beaker, and allowed to cool. Almost immediately crystals began to form. These crystals are needle-shaped and have a yellow tint. They group themselves in small bundles or sheaves. So great was the quantity of crystals that the mass soon became almost solid. The mother-liquor was removed by the aid of a filter-pump, and the crystals dried by pressing between folds of drying-paper. The crystals were labeled *A*.

To a second portion, 50 cc., of the potassium iodide solution, after heating, was added 10 grams of lead bromide. Crystals similar to *A* were obtained, though not in such large quantities. These were labeled *B*.

Still a third crop of crystals was obtained by dissolving 5 grams of lead bromide in 50 cc. of the heated potassium iodide solution. These crystals, labeled *C*, were similar in appearance to *A* and *B*, but the yield was much smaller.

Three portions, 50 cc. each, of the potassium iodide solution were then diluted, each with 50 cc. of water, and heated to boiling. To one of these portions was added 20 grams of lead bromide. The salt turned yellow, as above, but quite a large quantity failed to dissolve. After filtering from this undissolved portion, crystals were obtained from the solution similar to those prepared by using the more concentrated solution of potassium iodide. These crystals were labeled *A'*. To another portion of the diluted solution was added 10 grams of lead bromide. Practically all dissolved, and the needle-shaped crystals obtained on cooling were labeled *B'*. To a third portion of the diluted solution was added 5 grams of lead bromide. Crystals similar to the above were again obtained. These crystals were labeled *C'*.

10 grams of lead bromide were then added to 50 cc. of the concentrated solution of potassium iodide, but no heat applied. Some of the lead salt passed into solution on stirring the mass well, but some, having been changed to yellow lead iodide, remained undissolved. At the same time a white flocculent substance was formed just above the undissolved lead iodide, but it was found impossible to separate accurately the one from the other, so the mass was discarded. The supernatant liquid, however, gave birth to a small quantity of needle-shaped crystals (designated *D*)

after standing twenty-four hours, but the quantity was not sufficient for analysis. 50 cc. of water was then added to 50 cc. of the potassium iodide solution, and 10 grams of lead bromide added in the cold. The lead bromide immediately became yellow, showing the change to lead iodide, and now, after constant stirring, all of the lead iodide disappeared, and in its place was quite a large quantity of a flocculent, white substance, similar to that obtained in the preceding experiment. This salt was dried and labeled *X*.

In the mother-liquor from *X* there crystallised, on standing over night, very long, slender needles. These were labeled *D'*.

To each of the mother-liquors from *A*, *B*, *C* and *D* was then added 50 cc. of water. All were stirred thoroughly and allowed to stand. Large quantities of needle-shaped crystals separated in each case, and were labeled respectively *F*, *G*, *H* and *E*.

To the mother-liquors from *A'*, *B'*, *C'*, *D'*, *E*, *F*, *G* and *H*, water was added until the point of decomposition of the solution with setting free of lead iodide was almost reached. This was done by drawing off about 10 cc. of the solution, then diluting with water until lead iodide began to separate: now, on replacing the removed portion, the solution again became clear. In this way eight new crops of crystals were obtained. These were labeled *I*, *J*, *K*, *L*, *M*, *N*, *O* and *P*.

To the mother-liquors from each of these last was then added 50 cc. of absolute alcohol. Quite large crops of crystals were again obtained, and labeled *I'*, *J'*, *K'*, *L'*, *M'*, *N'*, *O'* and *P'*. The mother-liquors from these last were then evaporated to dryness.

Twenty-eight compounds had now been prepared from solutions containing varying quantities of lead bromide and potassium iodide. Furthermore, the proportion of water present had been varied, and finally a series obtained by the addition of alcohol. It was hoped that somewhere in this series of compounds the bromiodoplumbite would be found, but on carefully testing each one qualitatively, it was found that all of the compounds contained iodine, while not one of the twenty-eight showed the slightest trace of bromine. The residues obtained by evaporating the final mother-liquors to dryness showed the presence of both iodine and bromine. Evidently, only potassium iodo-plumbite had been formed in each case.

It has been shown[1] that most probably the only potassium iodoplumbite which can exist has the formula $KPbI_3.2H_2O$. To test again the correctness of this view, quantitative analyses were made of the compound *B'*, prepared from a hot solution, and the compound *X*, prepared in the cold. In *X*, only water and lead were determined, the lead being converted directly into the sulphate by treatment with sulphuric acid. Complete analyses of *B'* were made according to the method described above.

I. 0.7634 gram of *X* lost 0.0401 gram of water and yielded 0.3513 gram of lead sulphate = 0.2399 gram of lead.

II. 0.5304 gram of *X* lost 0.0269 gram of water and yielded 0.2425 gram of lead sulphate = 0.1656 gram of lead.

	I.	II.	Calculated for $KPbI_3.2H_2O$.
H_2O	5.25	5.07	5.43 per cent.
Pb	31.43	31.22	31.23 "

I. 1.0329 grams of *B'* gave 0.0544 gram of H_2O.
0.4698 gram of $PbSO_4$ = 0.3208 gram Pb.
1.1023 grams of AgI = 0.5956 gram I.
0.3965 gram of K_2PbCl_6 = 0.0639 gram K.

II. 1.0032 grams of *B'* gave 0.0531 gram of H_2O.
0.4562 gram of $PbSO_4$ = 0.3115 gram Pb.
1.0677 grams of AgI = 0.5769 gram I.
0.3893 gram of K_2PbCl_6 = 0.0627 gram K.

	I.	II.	Calculated for $KPbI_3.2H_2O$.
H_2O	5.27	5.29	5.43 per cent.
Pb	31.06	31.05	31.23 "
I	57.66	57.51	57.43 "
K	6.19	6.25	5.91 "
	100.18	100.10	100.00 "

Solution of Lead Iodide in Potassium Bromide.

Preliminary Experiments.—Having obtained only potassium iodoplumbite, $KPbI_3.2H_2O$, on dissolving lead bromide in an aqueous solution of potassium iodide, it was decided to change the conditions of experiment and dissolve lead iodide in a solution of potassium bromide. To this end a solution of potassium bromide was prepared by dissolving 190 grams of potassium bromide in

[1] This Journal **14**, 107.

350 cc. of water. Three portions, 50 cc. each, of this solution, labeled respectively *A*, *B* and *C*, were heated almost to boiling. To *A* was added 20 grams of lead iodide. Solution was effected quite readily. On cooling, needle-shaped crystals separated in such large quantities that the mass became almost solid. The possibility of the presence of alkaline halide as an impurity was so great that it was decided not to analyse this compound. To *B* was added 10 grams of lead iodide, all dissolved, and, on cooling, crystals, similar in appearance to those in *A*, were formed, but not in such large quantity. The mother-liquor was pumped off and the crystals dried as before, and labeled *B*. To *C* was added 5 grams of lead iodide. No crystals formed in this solution, either after cooling or after standing several days.

To try the effect of using a more dilute solution of potassium bromide, three portions, 50 cc. each, of the solution used in the preceding experiments were labeled respectively *A'*, *B'* and *C'*. To each was added 50 cc. of water and all were then heated to boiling. To *A'* was added 20 grams of lead iodide, to *B'* 10 grams and to *C'* 5 grams. In the case of *A'*, only a portion of the lead iodide dissolved, even after continued boiling, so the mass was set aside without filtering. Soon, crystals of lead iodide began to form. After standing twenty-four hours there were found in the vessel the red crystals of lead iodide, white needles similar to *A* and *B* above, and a third substance having the appearance of black specks in the mass. On examination with the microscope these last were found to be distinct crystals, dark green in color. After standing several days all the crystals in the vessel changed to white needles. In *B'* all of the lead iodide dissolved, though quite slowly. On cooling, lead iodide first crystallised out of the solution. After standing twenty-four hours there were found, as in *A'*, crystals of lead iodide, white needles, and the tabular green crystals. The last were much better developed than in *A'*. No separation could be made for analysis. In *C'* the lead iodide dissolved quite readily. After standing twenty-four hours, only the green tabular crystals were found in the solution. These were dried and labeled *C'*. In form they resemble closely potassium bromoplumbite.[1]

The compounds *B* and *C'* showed, by qualitative tests, the presence of both iodine and bromine. An addition of water to the

[1] This Journal **14**, 124.

mother-liquor from *B* caused the separation of a large quantity of needle-shaped crystals. These were not analysed. An addition of alcohol to the mother-liquor from *C'* caused the separation of a flocculent white compound. This compound was dried and labeled *C''*.

1.1812 grams of *B* gave 1.2943 grams of AgI and AgBr. This was transformed into 0.8995 gram of AgCl, which gives in original substance 0.3123 gram of I and 0.3049 gram of Br.

0.6729 gram of *C'* gave 0.7325 gram of AgI and AgBr. This was transformed into 0.5320 gram of AgCl, which gives in original substance 0.0956 gram of I and 0.2365 gram of Br.

0.8470 gram of *C''* gave 0.9355 gram of AgI and AgBr. This was transformed into 0.6688 gram of AgCl, which gives in original substance 0.1601 gram of I and 0.2720 gram of Br.

	B.	*C'.*	*C''.*	Calculated for $PbI_2.KBr$.	Calculated for $PbBr_2.KI$.
I	26.44	14.21	18.90	43.77	23.81 per cent.
Br	25.81	35.15	32.11	13.79	30.01 "

Series of Isomorphous Mixtures prepared by Dissolving Lead Iodide in an Aqueous Solution of Potassium Bromide.

Up to this point in the investigation, it has been shown that when lead bromide is dissolved in a somewhat concentrated solution of potassium iodide, only potassium iodoplumbite, $KPbI_3.2H_2O$, crystallises from the solution. On the other hand, it has been shown that when lead iodide is dissolved in solutions of potassium bromide of varying concentration, compounds are formed which show varying proportions of iodine and bromine. These proportions seem to vary according to the proportions of iodine and bromine in the solutions from which the salts crystallised. The composition of these compounds does not correspond to either of the simple formulas $KPbI_2Br$ ($PbI_2.KBr$) or $KPbIBr_2$ ($PbBr_2.KI$). These facts suggest that the compounds are isomorphous mixtures of potassium iodoplumbite and potassium bromoplumbite. To test this view, and, if correct, to determine what must be the composition of a solution from which a compound of a given composition is formed, the following experiments were made. All materials used in these experiments were kept in a warm closet at the uniform temperature of 29° C. The potassium-bromide solution used was made by dissolving 268 grams of the

salt in 400 cc. of water. 50 cc. of this solution contained 28.15 grams of potassium bromide and 41.85 grams of water.

Experiments with concentrated solutions of potassium bromide.—Three portions, 50 cc. each, of the potassium bromide solution mentioned above were heated almost to boiling. These were labeled *A*, *B* and *C*. To *A* was added 11 grams of lead iodide, to *B* 10 grams and to *C* 9 grams. The lead iodide dissolved in each case. The percentage composition of these hot solutions is given in the table below. After one hour, needle-shaped crystals began to form in *A*. Similar crystals began to form in *B* after two hours. Only after standing twenty-four hours did crystals begin to form in *C*. These crystals were similar to those in *A* and *B*. All three solutions were allowed to stand five days. The crystals were then dried and labeled respectively *A*, *B* and *C*. About 5 cc. of the mother-liquor from each was drawn off into a crucible and analysed. These portions were labeled respectively *A'*, *B'* and *C'*. To the remainder of the mother-liquors water was added until the point of decomposition with setting free of lead iodide was almost reached. In this way to the mother-liquor from *A* was added 21 cc. of water; to that from *B*, 25 cc.; and finally, to that from *C*, 25 cc. White needle-shaped crystals began to separate immediately in each vessel. After standing six hours the crystals were dried and labeled *A'*, *B'* and *C'*. A portion of the mother-liquor from each of these was analysed as before. These portions were labeled *A''*, *B''* and *C''*. To the main portion of these mother-liquors was added absolute alcohol, until the point of decomposition of the solution was almost reached. In this way to the mother-liquor from the compound *A'* was added 12 cc. of absolute alcohol; to that from *B'*, 13.5 cc., and to that from *C'*, 18.5 cc. Large quantities of white, needle-shaped crystals again formed in each vessel. These were dried and labeled respectively *A''*, *B''* and *C''*.

Analyses of Mother-liquors.

7.7897 grams of *A'* gave 3.8026 grams of H_2O.

0.4812 gram of $PbSO_4 = 0.3286$ gram of Pb.

5.8235 grams of AgI and AgBr. This was transformed into 4.3010 grams of AgCl, which gives in original solution 0.5069 gram I and 2.0792 grams Br.

6.5905 grams of $K_2PtCl_6 = 1.0617$ grams of K.

7.7016 grams of *B'* gave 3.8369 grams of H_2O.

0.4461 gram of $PbSO_4$ = 0.3046 gram of Pb.

5.6110 grams of AgI and AgBr. This was transformed into 4.1535 grams of AgCl, which gives in original solution 0.4555 gram of I and 2.0292 grams of Br.

6.4375 grams of K_2PtCl_6 = 1.0371 grams of K.

7.7520 grams *C'* gave 3.8091 grams of H_2O.

0.4863 gram of $PbSO_4$ = 0.3321 gram of Pb.

5.7705 grams of AgI and AgBr. This was transformed into 4.2775 grams of AgCl, which gives in original solution 0.4470 gram of I and 2.1038 grams of Br.

6.5545 grams of K_2PtCl_6 = 1.0559 grams of K.

6.4912 grams of *A''* gave 4.3402 grams of H_2O.

0.1792 gram of $PbSO_4$ = 0.1224 gram of Pb.

3.2090 grams of AgI and AgBr. This was transformed into 2.3855 grams of AgCl, which gives in original solution 0.2242 gram of I and 1.1892 grams of Br.

3.7970 grams of K_2PtCl_6 = 0.6117 gram of K.

6.5163 grams of *B''* gave 4.3277 grams of H_2O.

0.2200 gram of $PbSO_4$ = 0.1502 gram of Pb.

3.2390 grams of AgI and AgBr. This was transformed into 2.4075 grams of AgCl, which gives in original solution 0.2280 gram of I and 1.1989 grams of Br.

3.7770 grams of K_2PtCl_6 = 0.6085 gram of K.

6.5499 grams of *C''* gave 4.3154 grams of H_2O.

0.2103 gram of $PbSO_4$ = 0.1436 gram of Pb.

3.3230 grams of AgI and AgBr. This was transformed into 2.4725 grams of AgCl, which gives in original solution 0.2242 gram of I and 1.2377 grams of Br.

3.9140 grams of K_2PtCl_6 = 0.6305 gram of K.

The figures under *A*, *B* and *C* in the table below represent the percentage composition of the solutions *A*, *B* and *C* mentioned above, and were calculated directly from the weights of water, potassium bromide and lead iodide used in making up the solution.

From the hot solutions *A*, *B* and *C* crystals separated on cooling, but from the mother-liquors *A'*, *B'*, *C'*, *A''*, *B''* and *C''* (see table below) crystals separated only after the addition of water and alcohol in the quantities already mentioned.

TABLE I.

	H_2O.	Pb.	I.	Br.	K.	Total.
A	51.67	6.10	7.48	23.33	11.42	100.00
B	52.31	5.61	6.89	23.63	11.56	100.00
C	52.98	5.11	6.28	23.92	11.71	100.00
A'	48.82	4.22	6.51	26.69	13.63	99.87
B'	49.82	3.96	5.91	26.35	13.47	99.51
C'	49.14	4.28	5.77	27.14	13.62	99.95
A''	66.86	1.89	3.45	18.32	9.42	99.94
B''	66.41	2.30	3.50	18.40	9.34	99.95
C''	65.88	2.19	3.42	18.90	9.63	100.02

Analyses of Compounds.

1.0012 grams of *A* gave 0.0313 gram of H_2O.

0.5320 gram of $PbSO_4$ = 0.3633 gram of Pb.

1.1073 grams AgI and AgBr. This was transformed into 0.7672 gram of AgCl, which gives in original substance 0.2756 gram of I and 0.2542 gram of Br.

0.4581 gram of K_2PtCl_6 = 0.0738 gram of K.

1.0015 grams of *B* gave 0.0315 gram of H_2O.

0.5343 gram of $PbSO_4$ = 0.3649 gram of Pb.

1.1058 grams AgI and AgBr. This was transformed into 0.7670 gram of AgCl, which gives in original substance 0.2727 gram of I and 0.2558 gram of Br.

0.4427 gram of K_2PtCl_6 = 0.0713 gram of K.

1.0058 grams of *C* gave 0.0313 gram of H_2O.

0.5374 gram of $PbSO_4$ = 0.3670 gram of Pb.

1.1133 grams of AgI and AgBr. This was transformed into 0.7726 gram of AgCl, which gives in original substance 0.2732 gram of I and 0.2586 gram of Br.

0.4560 gram of K_2PtCl_6 = 0.0735 gram of K.

1.0010 grams of *A'* gave 0.0307 gram of H_2O.

0.5334 gram of $PbSO_4$ = 0.3643 gram of Pb.

1.1041 grams of AgI and AgBr. This was transformed into 0.7674 gram AgCl, which gives in original substance 0.2666 gram of I and 0.2599 gram of Br.

0.4361 gram of K_2PtCl_6 = 0.0703 gram of K.

0.9150 gram of *B'* gave 0.0285 gram of H_2O.

0.4909 gram of $PbSO_4$ = 0.3352 gram of Pb.

1.0114 grams of AgI and AgBr. This was transformed into 0.7030 gram of AgCl, which gives in original substance 0.2440 gram of I and 0.2383 gram of Br.

0.4111 gram of K_2PtCl_6 = 0.0662 gram of K.

1.0075 grams of *C'* gave 0.0317 gram of H_2O.

0.5434 gram of $PbSO_4$ = 0.3711 gram of Pb.

1.1129 grams of AgI and AgBr. This was transformed into 0.7768 gram of AgCl, which gives in original substance 0.2568 gram of I and 0.2714 gram of Br.

0.4467 gram of K_2PtCl_6 = 0.0720 gram of K.

1.0017 grams of *A''* gave 0.0314 gram of H_2O.

0.5409 gram of $PbSO_4$ = 0.3694 gram of Pb.

1.1072 grams of AgI and AgBr. This was transformed into 0.7752 gram of AgCl, which gives in original substance 0.2473 gram of I and 0.2764 gram of Br.

0.4449 gram of K_2PtCl_6 = 0.0717 gram of K.

1.0031 grams of *B''* gave 0.0321 gram of H_2O.

0.5454 gram of $PbSO_4$ = 0.3725 gram of Pb.

1.1095 grams of AgI and AgBr. This was transformed into 0.7795 gram of AgCl, which gives in original substance 0.2384 gram of I and 0.2844 gram of Br.

0.4512 gram of K_2PtCl = 0.0727 gram of K.

1.0015 grams of *C''* gave 0.0315 gram of H_2O.

0.5471 gram of $PbSO_4$ = 0.3736 gram of Pb.

1.1083 grams of AgI and AgBr. This was transformed into 0.7833 gram of AgCl, which gives in original substance 0.2214 gram of I and 0.2973 gram of Br.

0.4514 gram of K_2PtCl_6 = 0.0727 gram of K.

TABLE II.

	H_2O.	Pb.	I.	Br.	K.	Total.
A	3.13	36.29	27.53	25.39	7.37	99.71
B	3.15	36.44	27.23	25.54	7.12	99.48
C	3.11	36.49	27.16	25.71	7.31	99.78
A'	3.07	36.39	26.63	25.96	7.02	99.07
B'	3.11	36.63	26.67	26.04	7.23	99.68
C'	3.15	36.83	25.49	26.94	7.15	99.56
A''	3.13	38.88	24.69	27.59	7.16	99.45
B''	3.20	37.13	23.77	28.35	7.25	99.70
C''	3.15	37.30	22.11	29.69	7.26	99.51

Experiments with dilute solutions of potassium bromide.—Three portions, 50 cc. each, of the potassium bromide solution, labeled *D*, *E* and *F*, were heated almost to boiling.

To *D* was added 6 grams of lead iodide, to *E* 5 grams, and to *F* 4 grams. The lead iodide dissolved in each case. The percentage composition of these solutions is as follows:

TABLE III.

	H_2O.	Pb.	I.	Br.	K.	Total.
D	72.85	2.15	2.62	15.03	7.35	100.00
E	73.44	1.80	2.21	15.14	7.41	100.00
F	74.03	1.45	1.78	15.27	7.47	100.00

After standing one hour and a half, small, olive-green crystals began to form in *D*. These crystals are generally tabular; sometimes they have the appearance of four-rayed stars. After three hours, crystals similar to those in *D* began to form in *E*. Only after standing two days did a few small tabular crystals form in *F*. All three solutions were allowed to stand five days. At the end of this time the crystals in *D* and *E* had grown somewhat larger, while those in *F* had passed back into solution. The crystals from *D* and *E* were dried and labeled *D* and *E*. A close inspection of the crystals *D* showed a few white needles beginning to form on the edges of some of the tabular crystals. Such as these were discarded.

It was impossible to obtain any satisfactory crystals by dilution of the solution *F* or the mother-liquors from *D* and *E*, owing to the ready separation of lead iodide.

Analyses of Compounds.

1.0004 grams of *D* gave 0.6576 gram of $PbSO_4$ = 0.4491 gram of Pb.

1.0922 grams of AgI and AgBr. This was transformed into 0.7839 gram AgCl, which gives in original substance 0.1762 gram I and 0.3260 gram of Br.

0.2831 gram of K_2PtCl_6 = 0.0456 gram of K.

0.9993 gram of *E* gave 0.6647 gram $PbSO_4$ = 0.4539 gram of Pb.

1.0917 grams AgI and AgBr. This was transformed into 0.7910 gram AgCl, which gives in original substance 0.1493 gram of I and 0.3470 gram of Br.

0.2791 gram of K_2PtCl_6 = 0.0450 gram of K.

TABLE IV.

	Pb.	I.	Br.	K.	Total.
D	44.89	17.61	32.59	4.56	99.65
E	45.42	14.94	34.72	4.50	99.58

Explanation of Analytical Results.

Composition of the needle-shaped crystals.—At the beginning of the investigation it was hoped salts such as $KPbI_2Br.xH_2O$ and $KPbIBr_2.xH_2O$ might be obtained. The calculated composition of these salts, assuming only one molecule of water of crystallisation to be present, is as follows:

	H_2O.	Pb.	I.	Br.	K.	
$KPbI_2Br.H_2O$	3.01	34.62	42.45	13.38	6.54	per cent.
$KPbIBr_2.H_2O$	3.27	37.57	23.03	29.03	7.10	"

All of the compounds prepared from concentrated solutions of potassium bromide are well formed, needle-shaped crystals, but they show variations in composition (see Table II), corresponding in a general way to the variations in the composition of the solutions from which they crystallised. This suggests that these compounds are isomorphous mixtures of the simple iodoplumbite and bromoplumbite. This view is rendered more probable by the fact that in the above series the percentages of lead and bromine increase, while that of iodine decreases. This increase in the amount of lead is to be expected, as there is 42.58 per cent. of lead in the salt $KPbBr_2$, and only 33.02 per cent. of lead in the salt $KPbI_2$.

Since the composition of the simple halo-plumbites corresponds to the formulæ $KPbI_2.2H_2O$[1] and $KPbBr_2.H_2O$,[2] it seemed reasonable to expect that the isomorphous mixtures should be made up of varying proportions of these two substances. As will be seen by the calculations below this is true, with the exception that the iodoplumbite has only 1 molecule of water of crystallisation.

The composition of the salts $KPbI_3.2H_2O$ and $KPbBr_3.H_2O$ is as follows:

	H_2O.	Pb.	I.	Br.	K.	
$KPbI_3.2H_2O$	5.43	31.23	57.43	...	5.91	per cent.
$KPbBr_3.H_2O$	3.57	41.06	...	47.61	7.76	"

Taking now the case of the compound *C* (Table II), the analytical error being least here, and assuming that this is an isomor-

[1] This Journal **14**, 110. [2] *Ibid.* 124.

phous mixture of $KPbI_3.2H_2O$ and $KPbBr_3.H_2O$, then the 27.16 per cent. of iodine, present as iodoplumbite, would require 2.57 per cent. of water, for in the salt $KPbI_3.2H_2O$ there is present 57.43 per cent. of iodine and 5.43 per cent. of water.

$$57.43 : 5.43 :: 27.16 : x = 2.57 \text{ per cent. of water.}$$

Similarly, the 25.71 per cent. of bromine would require 1.93 per cent. of water, for the salt $KPbBr_3.H_2O$ contains 47.61 per cent. of bromine and 3.57 per cent. of water.

$$47.61 : 3.57 :: 25.71 : x = 1.93 \text{ per cent. of water.}$$

The sum of these amounts of water, required on the above assumption, is 4.50 per cent. (2.57 + 1.93); but by analysis there was found only 3.11 per cent. of water.

Evidently the compound does not contain the common iodoplumbite $KPbI_3.2H_2O$ and bromoplumbite $KPbBr_3.H_2O$. This same calculation proves that the mixture cannot be $KPbI_3.2H_2O$ and $KPbBr_3$, for the 27.16 per cent. of iodine requires only 2.57 per cent. of water, if the iodine is present as $KPbI_3.2H_2O$, while there was actually found 3.11 per cent. Assuming now that the mixture is composed of $KPbI_3$ and $KPb_3.2H_2O$, then the 25.71 per cent. bromine in *C* would require 3.85 per cent. of water, for the salt $KPbBr_3.2H_2O$ contains 45.97 per cent. of bromine and 6.88 per cent. of water.

$$45.97 : 6.88 :: 25.71 : x = 3.85 \text{ per cent. of water.}$$

Plainly this is wrong. The assumption that the mixture is $KPbI_3$ and $KPbBr_3.H_2O$ is also false; for the 25.71 per cent. of bromine requires, according to this formula, only 1.93 per cent. of water, since the salt $KPbBr_3.H_2O$ contains 47.61 per cent. of bromine and 3.57 per cent. of water.

$$47.61 : 3.57 :: 25.71 : x = 1.93 \text{ per cent. of water.}$$

Finally, assume that the mixture is composed of the salts $KPbI_3.H_2O$ and $KPbBr_3.H_2O$. The composition of these salts is as follows:

	H_2O.	Pb.	I.	Br.	K.
$KPbI_3.H_2O$	2.79	32.10	59.04	...	6.07 per cent.
$KPbBr_3.H_2O$	3.57	41.06	...	47.61	7.76 "

Now, the 27.16 per cent. of iodine found in *C* would require 1.28 per cent. of water, and the 25.71 per cent. of bromine would require 1.93 per cent. of water, giving thus the total amount of water as 3.21 per cent., whereas there was actually found 3.11 per

cent. Continuing now the same method of calculation for lead and potassium as was made use of in the case of water, it is found that 27.16 per cent. of iodine requires 14.77 per cent. of lead, and 25.71 per cent. of bromine requires 22.17 per cent. of lead, giving a total of 36.94 per cent. There was found 36.49 per cent.

As to potassium, 27.16 per cent. of iodine requires 2.79 per cent. of potassium, and 25.71 per cent. of bromine requires 4.19 per cent. of potassium, giving a total of 6.98 per cent. There was found 7.31 per cent.

It will be noticed that, according to the above calculations, the quantity of lead found by analysis is 0.45 per cent. less than that required by calculation, and that the potassium found by analysis is 0.33 per cent. greater than that required by calculation. This is probably to be partially accounted for by experimental error: on the other hand, this variation is rather to be expected if the method of preparation of the salt be taken into consideration. On account of its ready decomposition by water the compound could not be washed free from the mother-liquor, but was dried as quickly as possible, by means of a filter-pump and pressing between folds of drying-paper. Very probably, therefore, a small amount of alkali halide from the mother-liquor remained on the surface of the crystals. If this be true, then the calculated results for lead should be higher than the amounts found by analysis, while the calculations for potassium should be low, for, according to the above calculations, the entire amount of each halide has been considered in the form of a halo-plumbite.

Taking all of the above facts into consideration, it seems most probable that the needle-shaped crystals are isomorphous mixtures of the two salts $KPbI_3.H_2O$ and $KPbBr_3.H_2O$.

Composition of the tabular crystals.—The compounds *D* and *E* (Table IV) show by their percentage composition that they cannot be isomorphous mixtures of the salts $KPbI_3.H_2O$ and $KPbBr_3.H_2O$. In the first place, they contain no water of crystallisation. The salt $KPbI_3$ contains 33.02 per cent. of lead, while the salt $KPbBr_3$ contains 42.58 per cent. of lead. In any isomorphous mixture of these two salts the percentage of lead must vary between the extremes 33.02 and 42.58. Therefore, as in *D* there is present 44.89 per cent. of lead, and in *E* 45.42 per cent., this explanation of the composition of the compounds is plainly wrong.

The large percentage of lead found suggests the possibility of the presence of free lead bromide or iodide. Assuming that in *D* there is present $KPbBr_3$ and PbI_2, then the 32.59 per cent. of bromine would require 28.11 per cent. lead, and the 17.61 per cent. of iodine would require 14.36 per cent. of lead, giving the total percentage of lead required by this hypothesis 42.47 per cent., whereas there was actually found 44.89 per cent. Furthermore, the 32.59 per cent. of bromine would require 5.31 per cent. of potassium, but there was found only 4.56 per cent. This hypothesis must therefore be discarded. Again, assuming that the crystals are composed of $KPbI_3$ and $PbBr_2$, then the 17.61 per cent. of iodine would require 1.81 per cent. of potassium. As 4.56 per cent. was found, this view is wrong.

The large percentage of lead suggests two other possible explanations of the composition of the tabular crystals, namely, a mixture of $KPbI_3$, $KPbBr_3$ and PbI_2 or a mixture of $KPbI_3$, $KPbBr_3$ and $PbBr_2$. The first of these has already been shown to be false, for if all of the bromine is present as bromoplumbite, then the 32.59 per cent. of bromine in *D* would require 5.31 per cent. of potassium, which is greater than the amount of potassium found, 4.56 per cent., and, according to this view, still more potassium should be present in the form of iodoplumbite. This leaves, as the only other explanation, the idea that the tabular crystals are composed of $KPbI_3$, $KPbBr_3$ and $PbBr_2$. Assume, now, that this is correct. In the compound *D*, the 17.61 per cent. of iodine, present as iodoplumbite, would require 9.57 per cent. of lead and 1.81 per cent. of potassium. Deducting these amounts from the total amounts found by analysis, there remains 2.75 per cent. of potassium as bromoplumbite, and 35.32 per cent. of lead as bromoplumbite and lead bromide. The 2.75 per cent. of potassium present as bromoplumbite requires 16.87 per cent. of bromine and 14.55 per cent. of lead. Deducting the 16.87 per cent. of bromine from the total amount of bromine, there is left 15.72 per cent. of bromine as lead bromide, and deducting the 14.55 per cent. of lead from the 35.32 per cent. of lead present as bromoplumbite and lead bromide, there remains 20.77 per cent. of lead as lead bromide. Now, lead bromide contains 56.40 per cent. of lead and 43.60 per cent. bromine. Therefore the 20.77 per cent. of lead would require, to form lead bromide, 16.06 per cent. of bromine. By the above calculation there was found 15.72 per cent. of bromine.

The fact that in this last calculation, after deducting those amounts of the mixture present as potassium iodoplumbite and potassium bromoplumbite, the remaining lead and bromine are in the proportions necessary to form lead bromide, suggests the possibility that these tabular crystals are composed of $KPbI_3$ and KPb_2Br_5 ($2PbBr_2.KBr$). Now, KPb_2Br_5 is composed of 48.53 per cent. of lead, 46.88 per cent. of bromine and 4.59 per cent. of potassium. Accordingly, the 35.32 per cent. of lead remaining in *D*, after deducting the amount present as iodoplumbite, would require 34.12 per cent. of bromine and 3.34 per cent. of potassium, but there was found by analysis only 32.59 per cent. of bromine, and, after deducting from the total amount of potassium, 4.56 per cent., that present as iodoplumbite, 1.81 per cent., there remains only 2.75 per cent. of potassium. That this hypothesis is wrong can best be shown by another form of calculation. Assume that in these crystals all bromine is present as KPb_2Br_5, which for purposes of calculation can be written ($KPbBr_3.PbBr_2$). Then in that method of calculation based upon the assumption that these crystals are composed of $KPbI_3$, $KPbBr_3$ and $PbBr_2$, the ratio between the calculated amounts of $KPbBr_3$ and $PbBr_2$ should be a constant. This constant is that expressing the ratio between the molecular weights of $KPbBr_3$, 484.7, and $PbBr_2$, 356.91, and its numerical value is 0.7549. Now, *D* contains 34.17 per cent. of $KPbBr_3$ and 36.49 per cent. of $PbBr_2$. The ratio here is 1.0679, instead of 0.7549, as required by the hypothesis. By similar calculations the ratio in the salt *E* (Table II) is 1.0328. Another compound, tabular in form, has been prepared which shows a ratio of 1.3579.

From all of the above calculations it seems fair to conclude that the tabular crystals are mixtures of varying proportions of potassium iodoplumbite, $KPbI_3$, potassium bromoplumbite, $KPbBr_3$, and lead bromide, $PbBr_2$.

Compounds formed from Solutions containing Increasing Quantities of Iodine and Decreasing Quantities of Bromine.

As it had been found in the first part of the investigation (see section "Solution of Lead Bromide in Potassium Iodide") that when iodine is largely in excess of bromine only the iodoplumbite crystallised from the solution, the investigation was then directed

towards the determination of the point at which the bromoplumbite ceased to crystallise from the solution.

21.34 grams of potassium bromide and 8.3628 grams of potassium iodide were dissolved in 40.95 grams of water. To this solution was added 8 grams of lead iodide, and the mass heated to boiling in a flask connected with an inverted condenser. After cooling slightly the solution was filtered from the small amount of insoluble substance remaining, and on further cooling needle-shaped crystals separated in large quantity. These were dried and labeled *A*. Qualitative tests showed the presence of both iodine and bromine in this compound.

Another compound, *B*, similar in appearance to *A*, was prepared by dissolving 9 grams of lead iodide in a solution of 15.34 grams of potassium bromide and 16.7256 grams of potassium iodide in 40.95 grams of water. This compound showed by qualitative test a large amount of iodine, but only a small quantity of bromine.

Finally, a third compound, *C*, similar to *A* and *B*, was prepared by dissolving 9 grams of lead iodide in a solution of 12.34 grams of potassium bromide and 20.907 grams of potassium iodide in 40.95 grams of water. This compound showed by qualitative tests the presence of a great quantity of iodine, but only a trace of bromine. So great was the quantity of crystals formed here that the mass became almost solid.

Analyses of Compounds.

1.0011 grams of *A* gave 0.0555 gram of H_2O.

0.4705 gram of $PbSO_4$ = 0.3213 gram of Pb.

1.0668 grams of AgI and AgBr. This was transformed into 0.6774 gram of AgCl, which gives in original substance 0.4847 gram of I and 0.0722 gram of Br.

0.4014 gram of K_2PtCl_6 = 0.0647 gram of K.

1.0027 grams of *B* gave 0.0551 gram of H_2O.

0.4621 gram of $PbSO_4$ = 0.3156 gram of Pb.

1.0656 grams of AgI and AgBr. This was transformed into 0.6636 gram of AgCl, which gives in original substance 0.5304 gram of I and 0.0357 gram of Br.

0.3861 gram of K_2PtCl_6 = 0.0622 gram of K.

1.0020 grams of *C* gave 0.0543 gram of H_2O.

0.4571 gram of $PbSO_4$ = 0.3122 gram of Pb.

1.0642 grams of AgI and AgBr. This was transformed into 0.6585 gram of AgCl, which gives in original substance 0.5445 gram of I and 0.0240 gram of Br.

0.3934 gram of K_2PtCl_6 = 0.0634 gram of K.

TABLE V.

	H_2O.	Pb.	I.	Br.	K.	Total.
A	5.54	32.09	48.42	7.21	6.46	99.72
B	5.50	31.48	52.90	3.56	6.20	99.64
C	5.42	31.16	54.34	2.40	6.33	99.65

From these results it is evident that the point at which the iodoplumbite alone separates from the solution has almost been reached. The investigation was not carried further in this direction, because it has already been shown that if the ratio of iodine to bromine be sufficiently large, only the iodoplumbite is formed.

Furthermore, it was deemed unsafe to extend the experiments using the same weights of water, lead and potassium, for, even in *C*, so great a quantity of crystals formed, and there was consequently so great a concentration of the solution by water being taken up as water of crystallisation, that alkaline halide crystallised from the solution along with the needles. This is shown, in Table V, by the increase in the percentage of potassium in *C* over that in *B*. If no free potassium iodide or bromide had been present the percentage would have been less in *C* than in *B*.

From an examination of the percentages of water in Table V, it is seen that when the iodoplumbite is present in the mixture in much larger quantity than the bromoplumbite, the compound no longer has one molecule of water of crystallisation, but two molecules.

Compounds formed from Solutions containing Decreasing Quantities of Iodine and Increasing Quantities of Bromine.

In this series of experiments the same weights of potassium bromide were dissolved in constant quantities of water, but gradually increasing quantities of the lead iodide used in the first experiment were replaced by equivalent quantities of lead bromide, consequently the proportions of iodine and bromine alone varied.

A. 27.35 grams of potassium bromide was dissolved in 40.95 grams of water. After heating nearly to boiling, 9 grams of lead

iodide was added. From this solution needle-shaped crystals separated. These were dried and labeled *A*.

B. 27.35 grams of potassium bromide was dissolved in 40.95 grams of water, and, after heating, 5.00 grams of lead iodide and 3.1854 grams of lead bromide were added. On cooling, crystals similar to *A* separated from the solution. These were dried and labeled *B*.

Analyses of Compounds.

1.0005 grams of *A* gave 0.0320 gram of H_2O.

0.5363 gram of $PbSO_4 = 0.3662$ gram of Pb.

1.1037 grams of AgI and AgBr. This was transformed into 0.7680 gram of AgCl, which gives in original substance 0.2633 gram of I and 0.2623 gram of Br.

0.4466 gram of $K_2PtCl_6 = 0.0719$ gram of K.

1.0021 grams of *B* gave 0.0333 gram of H_2O.

0.5542 gram of $PbSO_4 = 0.3785$ gram of Pb.

1.1078 grams of AgI and AgBr. This was transformed into 0.7919 gram of AgCl, which gives in original substance 0.1894 grams of I and 0.3223 gram of Br.

0.4675 gram of $K_2PtCl_6 = 0.0753$ gram of K.

TABLE VI.

	H_2O.	Pb.	I.	Br.	K.	Total.
A	3.20	36.60	26.32	26.22	7.19	99.53
B	3.32	37.77	18.90	32.16	7.51	99.66

From these figures it is readily seen that *B* contains much more bromoplumbite than does *A*.

C. 27.35 grams of potassium bromide was dissolved in 40.95 grams of water. To the hot solution was added 3.00 grams of lead iodide and 4.7781 grams of lead bromide. Needle-shaped crystals again separated in small bundles resembling chestnut-burrs. These crystals were not analysed quantitatively, but showed by qualitative tests the presence of both iodine and bromine.

D. 27.35 grams of potassium bromide was dissolved in 40.95 grams of water. This solution was heated to boiling, and 2.00 grams of lead iodide and 5.5745 grams of lead bromide added. On cooling, white lath-shaped crystals separated. On treating these crystals with water they become yellow, showing still the presence of iodoplumbite in the compound.

E. Finally, 27.35 grams of potassium bromide were dissolved in 40.95 grams of water, and, after heating, 0.5 gram of lead iodide and 6.769 grams of lead bromide added. On cooling, crystals separated. These crystals were transparent, and resembled somewhat crystals of potassium bromide. After thorough drying, one of these transparent crystals was placed in a drop of water, and with the aid of a magnifying glass it was seen to become opaque as soon as the water came in contact with it. The crystal failed to dissolve, even after long standing. This was evidently a double salt, or rather a mixture of two, for qualitative tests show the presence of a slight quantity of iodine and large quantities of bromine. Thus it is seen that iodine, even when present in the solution in slightest quantities, makes up part of the compound which crystallises from the solution; differing thus from bromine in the presence of large proportions of iodine.

Further Proof of the Presence of Free Lead Bromide in the Tabular Crystals.

In the preceding section it has been shown that the iodoplumbite has a much greater tendency to form and separate from the solution than the bromoplumbite. It is probable, therefore, that when lead iodide is dissolved in a concentrated solution of potassium bromide, the first change which takes place is an exchange of bromine and iodine between part of the lead and part of the potassium. This is continued until equilibrium is established in that portion of the solution consisting of iodoplumbite and potassium iodide. As a result of this, there now remains in the rest of the mass a smaller quantity of potassium bromide and some lead bromide. Equilibrium is now established in this part of the solution. On cooling, the compound which crystallises contains, therefore, the excess of iodoplumbite and bromoplumbite held in solution by potassium iodide and potassium bromide, respectively.

It has been shown[1] that lead bromide is much less soluble in potassium bromide than is lead iodide in potassium iodide solution. Furthermore, all of the experiments on this subject show that the lead halides are much less soluble in dilute than in concentrated solutions of potassium halides. From these facts it is rather to be expected that when lead iodide is dissolved in a dilute solution of potassium bromide, the lead bromide formed in the

[1] This Journal **14**, 126.

exchange of halogens is more than sufficient to establish equilibrium with this dilute solution of potassium bromide. Consequently, on cooling, the excess of lead bromide would separate from the solution along with the iodoplumbite and bromoplumbite. If this be true, then the presence of a slightly larger quantity of potassium bromide in the solution should prevent the separation of free lead bromide, and only needle-shaped crystals, which have been shown to be mixtures of iodoplumbite and bromoplumbite, should crystallise from the solution. The following experiments seem to confirm this reasoning:

27.35 grams of potassium bromide was dissolved in 67.88 grams of water. After heating, 9 grams of lead iodide was dissolved in the solution. On cooling, tabular crystals separated.

0.9993 gram of this compound gave 0.6419 gram of $PbSO_4$ = 0.4384 gram of Pb.

1.0922 grams of AgI and AgBr. This was transformed into 0.7710 gram of AgCl, which gives in original substance 0.2218 gram of I and 0.2901 gram of Br.

0.2752 gram of K_2PtCl_6 = 0.0443 gram of K.

		By Calculation.	
Pb = 43.87	per cent.	$KPbI_3$ = 36.55	per cent.
I = 22.20	"	$KPbBr_3$ = 26.71	"
Br = 29.03	"	$PbBr_3$ = 36.27	"
K = 4.43	"		
Total = 99.53	"	Total = 99.53	"

Now, using the same quantities of water and lead iodide as used in the above experiment, but increasing the weight of potassium bromide from 27.35 grams to 32.35 grams, solution was effected by heating. From this solution, on cooling, only needle-shaped crystals separated, confirming thus the views expressed above. Here the solution was concentrated by the addition of potassium bromide.

This could also be effected by using a smaller quantity of water for the solution of the 27.35 grams of potassium bromide used in the first experiment. These conditions have already been complied with (Experiment *A*, p. 101) and only needle-shaped crystals obtained. The analysis of these needles shows them to be composed of only potassium iodoplumbite and potassium bromoplumbite.

University of Georgia.

ON THE DECOMPOSITION OF DIAZO COMPOUNDS.[1]

IV.—THE ACTION OF ETHYL ALCOHOL ON PARADIAZOTOLUENESULPHONIC ACID UNDER DIFFERENT PRESSURES.

By Ira Remsen and Paul J. Dashiell.

In the first article[2] in this series it was shown that the nature of the reaction that takes place when ethyl alcohol and paradiazotoluenesulphonic acid are heated together varies with the pressure. Experiments were made under pressures from 90 mm. to 500 mm. of mercury, and the following paragraph, quoted from the article referred to, sums up the results reached: "The experiments above described show that the higher the pressure the larger the proportion of ethoxy compound formed, and the lower the pressure the larger the proportion of toluenesulphonic acid formed."

"Under high pressure the reaction takes place as represented in this equation:

$$C_6H_3\begin{cases}CH_3\\SO_3\\N_2\end{cases}> + C_2H_5OH = C_6H_3\begin{cases}CH_3\\SO_3H\\OC_2H_5\end{cases} + N_2.$$

While at low pressure it takes place according to this equation:

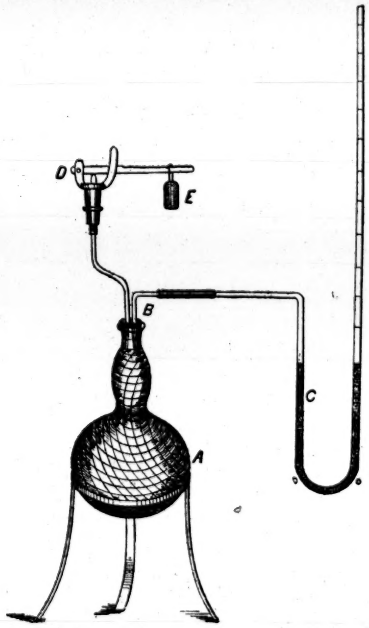
$$C_6H_3\begin{cases}CH_3\\SO_3\\N_2\end{cases}> + C_2H_5OH = C_6H_4<\begin{matrix}CH_3\\SO_3H\end{matrix} + N_2 + C_2H_4O."$$

Although the conclusions stated were undoubtedly justified, still the work was not very satisfactory as regards the details, and it seemed desirable to study the reactions more thoroughly, in the hope that the effect of the pressure on the course of the reaction might be followed more closely. We were fortunate enough to find a fairly satisfactory method of separating the products of the reactions, and thus of determining the relative quantity of each formed under different conditions. While the effect of change of pressure was the main point that we kept in view, the effect of the addition of water to the alcohol in various proportions was also studied.

[1] For the articles I, II, and III, see This Journal **8**, 243; **9**, 387, and **11**, 319.

[2] *Loc. cit.* **8**, 243.

The diazo compound used was prepared by us starting with paranitrotoluene. There is no difficulty if the methods described by Beilstein and Kuhlberg[1] for the nitrotoluenesulphonic acid, of Brackett and Hayes[2] for the amidotoluenesulphonic acid, and of De Roode[3] for the diazo compound are followed.



Apparatus.—The apparatus used in the experiments is that shown in the figure. It consists of the following parts: A strong balloon flask (*A*) of 1½ litres capacity is covered with a close network of copper wire. The flask is fitted with a two-hole rubber stopper, which is bound down by wire during the experiment. Into one of the holes is fitted a bent glass tube (*B*)

[1] Annalen der Chemie **155**, 8. [2] This Journal **9**, 399. [3] *Ibid.* **13**, 219.

connecting with an open end U-tube mercury manometer, graduated in millimeters. Into the other hole through the stopper is fitted a copper tube, at the top of which is a conical valve provided with a lever, on which is hung a leaden weight. By adjusting this weight properly and keeping up a gentle heat, the contents of the flask can be kept boiling at any desired pressure, until the reaction is finished, the variations of the manometer not exceeding five to ten millimeters. In decomposing at high pressures, the precaution was taken to heat rapidly and thus raise the pressure to the desired point as quickly as possible, for the purpose of avoiding the reactions at lower pressures.

Method of Separating the Two Products.

After the decomposition of the diazo compound with alcohol, there are two products in solution in the excess of alcohol, viz., orthotoluenesulphonic acid and ethoxytoluenesulphonic acid. After evaporating off the alcohol, the residue was dissolved in water and neutralised with barium carbonate. The filtered solution of the two barium salts was then evaporated to dryness on the water-bath. It was found that the ethoxy barium salt is but slightly soluble in cold 94-per cent. alcohol, and far more soluble at the boiling-point, while the salt of orthotoluenesulphonic acid is but little soluble in boiling alcohol. Upon these facts the following method of separation rests. To the united portions of the barium salts a convenient quantity of alcohol was added, and the temperature raised to boiling for a few minutes. The solid matter was allowed to settle, the solution decanted into a beaker, and the process repeated. The decanted portions were raised to boiling and passed through a weighed filter. The residue in the flask was then boiled with a third portion of alcohol, and thrown on the same filter. These repeated partial extractions were necessary on account of the ready deposition of the ethoxy salt on slight cooling of its solution in alcohol. The filtrate was evaporated to dryness on the water-bath. The residue was dried at 100° C. in the air-bath. A determination of barium was made in each product.

As an example of the results obtained the following is given:

Weight of barium salts,	9.1 grams.
[A] Weight of portion extracted by alcohol,	3.6
[B] Weight of residue,	5.3

Analysis of [A].—0.2188 gram of anhydrous salt gave 0.0913 gram of barium sulphate.

	Calculated for $C_6H_3\begin{cases}CH_3\\SO_3ba\\O.C_2H_5\end{cases}$.	Found.
Ba	24.16	24.49

Analysis of [B].—0.2332 gram of anhydrous salt gave 0.1129 gram of barium sulphate.

	Calculated for $C_6H_4\begin{cases}CH_3\\SO_3ba\end{cases}$.	Found.
Ba	28.60	28.42

The method of separation is quite good, as shown by the results of more than forty experiments. Moreover, the transformation of the two products of separation into derivatives of ethoxytoluenesulphonic acid on the one hand, and of toluenesulphonic acid on the other, furnished direct evidence of its efficacy. A constant check was kept on the general results obtained by extraction, by analyses of the products.

As a point of interest in this connection, the exact solubilities of the two barium salts were determined. The crude products were recrystallised until their analyses showed them to be pure. The apparatus used in the determinations of solubility was constructed after the manner of that described by Victor Meyer.[1] Three experiments were made for the purpose of determining the solubility of each salt in alcohol at the boiling-point. The mean results showed that—

100 grams of 94-per cent. alcohol dissolve 0.230 gram of barium orthotoluenesulphonate.

100 grams of 94-per cent. alcohol dissolve 5.5 grams of barium para-ethoxyorthotoluenesulphonate.

The latter is, therefore, more than twenty times more soluble than the former.

Method of Work.

In the work to be described, a series of three experiments was made under each particular set of conditions under investigation. The exact method of procedure was as follows: A weighed quantity of the diazo compound (about 10 grams) was introduced into the dry flask together with 200 cc. of alcohol, and boiled under the conditions of pressure desired. The decomposition being complete, the contents of the flask were washed with alcohol

[1] Ber. d. chem. Ges. **8**, 998.

through a weighed filter, and the small quantity of undiazotised toluidinesulphonic acid (usually less than half a gram) dried and weighed. The figures given as representing the diazo compound in each case were obtained by subtracting this weight from the total introduced into the flask.

From the more or less colored filtrate the excess of alcohol was distilled off, leaving a dark, viscous mass. This was taken up in water, converted into the barium salts, the solution evaporated to dryness on the water-bath, and the two products separated as described above. In nearly all cases the quantity of alcohol used in the extraction was 250 cc. Care was taken to boil for the same length of time in the different experiments, and other precautions observed, in order that the results should be strictly comparable. In some cases this quantity of alcohol was insufficient for the solution of all the ethoxy salt, and more was used. In others it was excessive, but mention will be made of these points when the experiments are described. In each series of experiments, analyses were made of the separated products. In case the relative weights of the latter were found to be nearly the same for the three experiments in any series, analyses were made in but one case. If discrepancies occurred greater than might have been expected from the comparatively rough method of separation used, examinations of the products were made in each case. These analyses furnished means of judging how far the separation had been successful, and in some cases were used as a basis for correcting the figures representing the products isolated.

I.—Decomposition of the Diazo Compound at Constant Pressure, the Strength of Alcohol being varied.

The pressure throughout these experiments was kept constant at 300 mm.

Experiments with Absolute Alcohol.—I. 9.5 grams of the diazo body were decomposed in 200 cc. of absolute alcohol. The odor of aldehyde was marked. The action continued about half an hour. The color of the solution passed through yellow to dull red. The barium salts showed a yellowish color in solution, but were free from color when dry.

Weight of barium salts,	12.15 grams.
[A] Weight of portion dissolved by alcohol,	5.10
[B] Weight of residue,	6.86

Analysis of [A].—0.2106 gram of anhydrous salt gave 0.0869 gram of barium sulphate.

	Calculated for $C_6H_3\begin{cases}CH_3\\SO_3ba\\O.C_2H_5\end{cases}$.	Found.
Ba	24.16	24.17

Analysis of [B].—0.2348 gram of anhydrous salt gave 0.1133 gram of barium sulphate.

	Calculated for $C_6H_4\begin{cases}CH_3\\SO_3ba\end{cases}$.	Found.
Ba	28.60	28.32

II. 10 grams of diazo compound were decomposed in 200 cc. of absolute alcohol. The same phenomena were noted as in the last experiment.

Weight of barium salts,	12.21 grams.
Weight of portion dissolved by alcohol,	4.80
Weight of residue,	7.31

III. 8.9 grams of diazo compound were decomposed in 200 cc. of absolute alcohol. Same phenomena as before.

Weight of barium salts,	11.28 grams.
Weight of portion dissolved by alcohol,	5.45
Weight of residue,	5.72

If an average be taken of the figures representing the three portions of the ethoxy compound and compared with that for the hydrogen products, we find that they stand in the relation of 5.08 to 6.63. Representing the sum of these as one hundred, the ethoxy body is found to constitute 43.4 per cent. It appears from these experiments that in decomposition of the diazo body at 300 mm. pressure, both hydrogen and ethoxy reactions take place, the former to the greater extent. The results obtained by Remsen and Palmer[1] led them to the conclusion that the ethoxy reaction is the principal one under these conditions.

It will be noticed in these experiments, as in other series, that the results are not closely concordant. The general tendency as indicated by the averages taken is, however, unmistakable, as will be seen later.

Experiments with 95-per cent. Alcohol.—I. 9.4 grams of diazo compound were decomposed in 200 cc. of 95-per cent. alcohol.

[1] Loc. cit.

The odor of aldehyde was strong. The reaction required about twenty minutes. The solution during and after the reaction showed deeper color than in cases where absolute alcohol was used. The barium salts dried showed faint yellow color.

Weight of barium salts,	12.02 grams.
[A] Weight of portion dissolved by alcohol,	4.45
[B] Weight of residue,	7.45

Analysis of [A].—0.2684 gram of anhydrous salt gave 0.1104 gram of barium sulphate.

	Calculated for $C_6H_3\begin{cases}CH_3\\SO_3ba.\\O.C_2H_5\end{cases}$	Found.
Ba	24.16	24.14

Analysis of [B].—0.2533 gram of anhydrous salt gave 0.1215 gram of barium sulphate.

	Calculated for $C_6H_4\begin{cases}CH_3\\SO_3ba.\end{cases}$	Found.
Ba	28.60	28.14

II. 9.7 grams of diazo compound were decomposed in 200 cc. of 95-per cent. alcohol. The same points were noticed as in the last experiment.

Weight of barium salts,	12.02 grams.
[A] Weight of portion dissolved by alcohol,	4.30
[B] Weight of residue,	7.60

Analysis of [A].—0.2664 gram of anhydrous salt gave 0.1179 gram of barium sulphate.

	Calculated for $C_6H_3\begin{cases}CH_3\\SO_3ba.\\O.C_2H_5\end{cases}$	Found.
Ba	24.16	24.63

Analysis of [B].—0.2444 gram of anhydrous salt gave 0.1179 gram of barium sulphate.

	Calculated for $C_6H_4\begin{cases}CH_3\\SO_3ba.\end{cases}$	Found.
Ba	28.60	28.65

These results indicate a fair separation.

III. 8.75 grams of diazo compound were decomposed in 200 cc. of 95-per cent. alcohol.

Weight of barium salts,	10.49 grams.
Weight of portion dissolved by alcohol,	3.4
Weight of residue,	6.9

Taking the averages of the figures representing the ethoxy and hydrogen products, we find that they stand in the relation of 4.05 to 7.28, indicating that the ethoxy product forms 35.8 per cent. of the total. It will be noticed that this figure is nearly 8 per cent. lower than that obtained when absolute alcohol was used in the decomposition.

Experiments with 90-per cent. Alcohol.—I. 9.8 grams of diazo compound were decomposed in 200 cc. of 90-per cent. alcohol. The odor of aldehyde was strong. The decomposition was more rapid than before, being complete in about fifteen minutes. The color of the solution was deeper than in any previous case. The barium salts dried, as well as the extracted ethoxy portion, showed more color than before.

Weight of barium salts,	12.38 grams.
[A] Weight of portion dissolved by alcohol,	5.40
[B] Weight of residue,	6.65

Analysis of [A].—0.2812 gram of anhydrous salt gave 0.1181 gram of barium sulphate.

	Calculated for $C_6H_3{<}^{CH_3}_{SO_3ba.}{}_{O.C_2H_5}$	Found.
Ba	24.16	24.66

Analysis of [B].—0.2444 gram of anhydrous salt gave 0.1223 gram of barium sulphate.

	Calculated for $C_6H_4{<}^{CH_3}_{SO_3ba.}$	Found.
Ba	28.60	28.26

II. 9 grams of diazo compound were decomposed in 200 cc. of 90-per cent. alcohol. The same phenomena were noted as in the preceding case.

Weight of barium salts,	10.98 grams.
Weight of portion dissolved by alcohol,	4.93
Weight of residue,	6.03

III. 9.75 grams of diazo compound were decomposed in 200 cc. of 90-per cent. alcohol.

Weight of barium salts,	12.00 grams.
Weight of portion dissolved by alcohol,	5.58
Weight of residue,	6.24

The averages, taken as before, for this series of experiments stand in the relation of 5.3 to 6.3, the ethoxy product constituting 45.7 per cent. of the total. From the relation of the results of the two preceding series a lower figure was expected. A smaller proportion of the ethoxy body was obtained in the experiments with 95-per cent. alcohol than when absolute alcohol was used. The marked presence of color in the products from this series of experiments is suggestive of other reactions than those under discussion. It is possible that the small amount of water present gave rise to phenol reactions. It may have been due to this fact that the separation of the products as indicated by the analyses was not so sharp as in preceding cases. The tendency here mentioned showed itself in greater degree when still more dilute alcohol was used in the decomposition.

Experiments with 85-per cent. Alcohol.—I. 9.9 grams of diazo compound were decomposed in 200 cc. of 85-per cent. alcohol. A strong odor of aldehyde was perceptible. The decomposition was complete in about twelve minutes. The color of the solution during the reaction was a muddy brown, changing to deep garnet-red as it neared completion. The dried barium salts showed yellow color. The extracted ethoxy salt was brownish red when dried.

Weight of barium salts,	12.02 grams.
[A] Weight of portion dissolved by alcohol,	6.14
[B] Weight of residue,	5.85

Analysis of [A].—0.2381 gram of anhydrous salt gave 0.1011 gram of barium sulphate.

	Calculated for $C_6H_3{<}^{CH_3}_{SO_3ba.}{}_{O.C_2H_5}$	Found.
Ba	24.16	25.04

Analysis of [B].—0.2545 gram of anhydrous salt gave 0.1229 gram of barium sulphate.

	Calculated for $C_6H_4{<}^{CH_3}_{SO_3ba}$.	Found.
Ba	28.60	28.57

The results show the portion [B] to have been very pure. Granting that the ethoxy salt was contaminated by the presence of some hydrogen salt only, the figures that would more nearly represent the relative quantities of the two products would be:

Weight of ethoxy salt, 5.23 grams.
Weight of hydrogen salt, 6.76

It is doubtful, from what was said under the preceding experiment, whether it is right to assume that the impurity consisted entirely of the hydrogen salt.

II. 10.2 grams of diazo compound were decomposed in 200 cc. of 85-per cent. alcohol. The decomposition was complete in ten minutes. The same color was noted in the products as in the preceding experiment.

Weight of barium salts,	12.43 grams.
[A] Weight of portion dissolved by alcohol,	4.57
[B] Weight of residue,	7.63

Analysis of [A].—0.2232 gram of anhydrous salt gave 0.0954 gram of barium sulphate.

	Calculated for $C_6H_3\begin{cases}CH_3\\SO_3ba\\O.C_2H_5\end{cases}$	Found.
Ba	24.16	25.08

Analysis of [B].—0.2435 gram of anhydrous salt gave 0.1143 gram of barium sulphate.

	Calculated for $C_6H_4\begin{cases}CH_3\\SO_3ba\end{cases}$	Found.
Ba	28.60	27.55

In this experiment it will be seen that the two products were not separated by boiling with alcohol in the usual way. In the cases in which strong alcohol was used in the decomposition, the dissolving action of the alcohol used in extraction was found to be sharp. If just the right quantity was used the separation was satisfactory. If too much was used, all the ethoxy product was dissolved together with some of the other, the analyses showing a high percentage of barium for the former, but nearly theoretical for the residue. If the quantity of alcohol was insufficient for the extraction of the ethoxy salt, the residual product showed a low percentage of barium, the ethoxy portion appearing pure. In either case one of the products seemed to be fairly pure. In the analyses just given it will be seen that neither product appears to have been pure, and it is probable that foreign matter was present, due to the dilution of the alcohol used in the decomposition.

III. 10 grams of diazo compound were decomposed in 200 cc. of 85-per cent. alcohol. The same facts were noted as in the last two decompositions.

Weight of barium salts,	12.44 grams.
Weight of portion dissolved by alcohol,	5.20
Weight of residue,	7.23

Although, for the reasons given, not too great reliance should be placed upon the results of the experiments of this series, it may be well to take the averages of the figures as obtained. They stand in the ratio of 4.99 to 7.20, the ethoxy compound representing 40.9 per cent. of the total. This figure lies between those found for cases in which absolute and 95-per cent. alcohols were used.

Experiments with 80-per cent. Alcohol.—The decompositions in 80-per cent. alcohol are of interest only in so far as they show to a greater degree the tendencies noticed in the last series. The decomposition was very rapid. The products were deeply colored. The separation by means of alcohol was entirely unsatisfactory. The extracted portions, on evaporation to dryness, showed a deep scarlet color. The relative quantities of the separated products differed so widely that no definite conclusions can be drawn from the three experiments made.

No further experiments were made on the influence of dilution of the alcohol on the reactions.

A brief summary of results follows:

Pressure constant. Strength of Alcohol used in decomposition.	Ethoxy Product.
Absolute	43.4 per cent.
Ninety-five per cent.	35.8
Ninety per cent.	47.7
Eighty-five per cent.	40.9
Eighty per cent.	...

The main conclusions from these experiments are as follows:

I. The presence of small quantities of water in the alcohol has little influence on the course of the reactions in the decomposition of the diazo compound.

II. The presence of more than 15 per cent. of water gives rise to other reactions than those involved in the decomposition of the diazo body to toluenesulphonic acid and to ethoxytoluenesulphonic acid. The formation of phenol bodies probably takes place. The fact that the decomposition in dilute alcohol is much more rapid than in strong alcohol is suggestive.

II.—Decomposition of the Diazo Compound in Absolute Alcohol, the Pressure being varied.

The lowest pressure at which Remsen and Palmer were able to obtain satisfactory results was 120 mm. The highest that could be measured by the manometer used in these experiments was 800 mm. Accordingly, eight series of decompositions were made at intervals of pressure between these limits. The experiments were conducted in the manner already described. The separation of the two products was effected by extraction with 250 cc. of 94-per cent. alcohol, except in cases of very high pressures, when this quantity was found insufficient.

Experiments at 120 *mm. Pressure.*—I. 9.5 grams of diazo compound were decomposed in 200 cc. of absolute alcohol. The odor of aldehyde was very strong. The action continued about forty minutes. There was considerable color in the solution during and after decomposition. But little color was noticeable in the dried barium salts.

Weight of barium salts,	11.62 grams.
[A] Weight of portion dissolved by alcohol,	4.3
[B] Weight of residue,	7.20

Analysis of [A].—0.2442 gram of anhydrous salt gave 0.1033 gram of barium sulphate.

	Calculated for $C_6H_3-SO_3ba.$ $\diagup CH_3$ $\diagdown O.C_2H_5$	Found.
Ba	24.16	24.84

Analysis of [B].—0.2416 gram of anhydrous salt gave 0.1166 gram of barium sulphate.

	Calculated for $C_6H_4<^{CH_3}_{SO_3ba}$.	Found.
Ba	28.60	28.33

It would appear that the number representing the ethoxy product was too great.

II. 10.2 grams of diazo compound were decomposed in 200 cc. of absolute alcohol. The same phenomena were noted as before.

Weight of barium salts,	12.22 grams.
Weight of portion dissolved by alcohol,	4.07
Weight of residue,	8.12

These figures correspond very nearly to those that would be obtained from the preceding experiment if correction were made according to the results of the analyses.

III. 9.3 grams of diazo compound were decomposed in 200 cc. of absolute alcohol.

Weight of barium salts,	11.26 grams.
Weight of portion dissolved by alcohol,	4.60
Weight of residue,	6.55

Although the results of this experiment differ considerably from those of the two preceding it, still in all three the hydrogen reaction is evidently the principal one. The averages stand in the ratio of 4.32 to 7.29, the ethoxy compound representing 37.2 per cent. of the total.

Experiments at 210 *mm. Pressure.*—I. 8 grams of diazo compound were decomposed in 200 cc. of absolute alcohol.

The points noted were practically the same as in the preceding series. The color of the solution was cherry red. The barium salts showed no color.

Weight of barium salts,	9.03 grams.
[A] Weight of portion dissolved by alcohol,	3.42
[B] Weight of residue,	5.44

Analysis of [A].—0.2386 gram of anhydrous salt gave 0.1005 gram of barium sulphate.

	Calculated for $C_6H_3\begin{cases}CH_3\\SO_3ba\\O.C_2H_5\end{cases}$.	Found.
Ba	24.16	24.72

Analysis of [B].—0.2493 gram of anhydrous salt gave 0.1209 gram of barium sulphate.

	Calculated for $C_6H_4\begin{cases}CH_3\\SO_3ba\end{cases}$.	Found.
Ba	28.60	28.47

II. 9.5 grams of the diazo body were decomposed in 200 cc. of absolute alcohol.

Weight of barium salts,	11.73 grams.
Weight of portion dissolved by alcohol,	4.54
Weight of residue,	7.11

The proportion of ethoxy product appeared so small that it seemed probable that all had not been extracted. The hydrogen portion was accordingly boiled with alcohol once more. Only about 0.3 gram was dissolved out.

III. 9 grams of diazo compound were decomposed in 200 cc. of absolute alcohol.

Weight of barium salts,	10.83 grams.
Weight of portion dissolved by alcohol,	4.70
Weight of residue,	5.97

The averages taken as before stand in the ratio 4.22 to 6.17, indicating that the ethoxy compound made 40.6 per cent. of the total.

Experiments at 300 *mm. Pressure.*—The decompositions in absolute alcohol at 300 mm. pressure have been discussed. They indicated that the ethoxy product constitutes 43.4 per cent. of the total.

Experiments at 400 *mm. Pressure.*—I. 9.6 grams of diazo compound were decomposed in 200 cc. of absolute alcohol. A strong odor of aldehyde was noticed. The decomposition was complete in a little less than half an hour. The other points noted were about as in the series at 300 mm. pressure.

Weight of barium salts,	11.74 grams.
[A] Weight of portion dissolved by alcohol,	5.75
[B] Weight of residue,	5.85

Analysis of [A].—0.2368 gram of anhydrous salt gave 0.0991 gram of barium sulphate.

	Calculated for $C_6H_3{<}^{CH_3}_{SO_3ba}{}_{O.C_2H_5}$	Found.
Ba	24.16	24.56

Analysis of [B].—0.2216 gram of anhydrous salt gave 0.1070 gram of barium sulphate.

	Calculated for $C_6H_4{<}^{CH_3}_{SO_3ba}$	Found.
Ba	28.60	28.34

II. 8.9 grams of diazo compound were decomposed in 200 cc. of absolute alcohol.

Weight of barium salts,	10.89 grams.
Weight of portion dissolved by alcohol,	5.37
Weight of residue,	5.41

III. 9.9 grams of diazo compound were decomposed in 200 cc. of absolute alcohol.

Weight of barium salts,	12.37 grams.
Weight of portion dissolved by alcohol,	5.72
Weight of residue,	6.41

The averages stand to each other as 5.61 to 5.89, the ethoxy compound constituting 48.7 per cent. of the total.

Experiments at 500 mm. Pressure.—I. 8.4 grams of diazo compound were decomposed in 200 cc. of absolute alcohol. The odor of aldehyde was not so strong as in previous experiments. The decomposition lasted about twenty minutes. There was less color in the solution during and after decomposition than before, and the dried barium salts were practically white.

Weight of barium salts, 10.58 grams.
[A] Weight of portion dissolved by alcohol, 4.40
[B] Weight of residue, 6.02

It was noticed, on extraction with alcohol, that the filtered portion, on cooling very slightly, deposited an unusually large quantity of crystalline ethoxy salt. This evident saturation of the solution raised doubt as to the completeness of the extraction of the ethoxy salt. The analyses of the products confirmed the doubt.

Analysis of [A].—0.2507 gram of anhydrous salt gave 0.1049 gram of barium sulphate.

	Calculated for $C_6H_3\begin{cases}CH_3\\SO_3ba\\O.C_2H_5\end{cases}$.	Found.
Ba	24.16	24.55

Analysis of [B].—0.2782 gram of anhydrous salt gave 0.1328 gram of barium sulphate.

	Calculated for $C_6H_4<\begin{matrix}CH_3\\SO_3ba\end{matrix}$.	Found.
Ba	28.60	28.01

Calculating from the analyses, the numbers that would more nearly represent the two weights would be:

Weight of ethoxy salt, 5.30 grams.
Weight of hydrogen salt, 5.12

II. 8.8 grams of diazo compound were decomposed in 200 cc. of absolute alcohol. The experiment was conducted in the same way as the preceding one, and with like results.

Weight of barium salts, 12.85 grams.
Weight of portion dissolved by alcohol, 5.92
Weight of residue, 6.8

The corrected numbers are:

Weight of ethoxy salt, 6.89 grams.
Weight of hydrogen salt, 5.83

III. 10.4 grams of diazo compound were decomposed in 200 cc. of absolute alcohol.

Weight of barium salts,	12.87 grams.
[A] Weight of portion dissolved by alcohol,	5.90
[B] Weight of residue,	6.82

Analysis of [A].—0.2772 gram of anhydrous salt gave 0.1152 gram of barium sulphate.

	Calculated for $C_6H_3\begin{cases}CH_3\\SO_3ba\\O.C_2H_5\end{cases}$	Found.
Ba	24.16	24.43

Analysis of [B].—0.2665 gram of anhydrous salt gave 0.1275 gram of barium sulphate.

	Calculated for $C_6H_4\begin{cases}CH_3\\SO_3ba\end{cases}$.	Found.
Ba	28.60	28.09

The corrected numbers would be:

Weight of ethoxy salt, 6.75 grams.
Weight of hydrogen salt, 5.97

The averages for this series stand in the ratio of 6.31 to 5.64, the ethoxy compound constituting 52.8 per cent. of the total.

This is the first series of experiments in which the ethoxy product was formed in greater quantity than the other. According to the results, the ethoxy reaction predominates over the other but very little. Remsen and Palmer were led to the conclusion that at this pressure it is the sole reaction.

Experiments at 600 *mm. Pressure.*—I. 9.3 grams of diazo compound were decomposed in 200 cc. of absolute alcohol. There was little odor of aldehyde perceptible. The decomposition was complete in about twelve minutes. There was less color in the products of decomposition than in any previous experiment.

Weight of barium salts,	11.84 grams.
Weight of portion dissolved by alcohol,	6.8
Weight of residue,	4.9

II. 8.8 grams of the diazo body were decomposed in 200 cc. of absolute alcohol. The same points were noted as in the preceding experiment.

Weight of barium salts,	11.22 grams.
Weight of portion dissolved by alcohol,	6.02
Weight of residue,	5.08

III. 10 grams of diazo compound were decomposed in 200 cc. of absolute alcohol.

Weight of barium salts,	12.21 grams.
[A] Weight of portion dissolved by alcohol,	7.3
[B] Weight of residue,	4.8

Analysis of [A].—0.2493 gram of anhydrous salt gave 0.1035 gram of barium sulphate.

	Calculated for $C_6H_3{<}^{CH_3}_{SO_3ba.}{>}O.C_2H_5$	Found.
Ba	24.16	24.37

Analysis of [B].—0.2327 gram of anhydrous salt gave 0.1117 gram of barium sulphate.

	Calculated for $C_6H_4{<}^{CH_3}_{SO_3ba}$.	Found.
Ba	28.60	28.16

It was found necessary in this series to increase the quantity of alcohol used in the separation to 300 cc. The averages of the weights of the two products obtained stand in the ratio of 6.7 to 4.9, the ethoxy compound constituting 57.7 per cent. of the total—a marked increase over the result of the last series of experiments.

Experiments at 700 mm. Pressure.—Four decompositions were made at this pressure.

I. 10.7 grams of diazo compound were decomposed in 200 cc. of absolute alcohol. A very faint odor of aldehyde was perceptible at the valve. The decomposition was complete in eight minutes. The solution after decomposition showed a light yellow color; the dried barium salts, none at all. It was necessary to use 350 cc. of alcohol in extracting the ethoxy salt.

Weight of barium salts,	10.73 grams.
[A] Weight of portion dissolved by alcohol,	6.74
[B] Weight of residue,	3.92

Analysis of [A].—0.2312 gram of anhydrous salt gave 0.0974 gram of barium sulphate.

	Calculated for $C_6H_3{<}^{CH_3}_{SO_3ba.}{>}O.C_2H_5$	Found.
Ba	24.16	24.72

Analysis of [B] was thought to be unnecessary.

II. 9.4 grams of diazo compound were decomposed in 200 cc. of absolute alcohol. The same phenomena were noted as in the preceding experiment.

Weight of barium salts,	11.34 grams.
Weight of portion dissolved by alcohol,	7.11
Weight of residue,	4.15

III. 9.6 grams of diazo compound were decomposed in 200 cc. of absolute alcohol.

Weight of barium salts,	12.36 grams.
Weight of portion dissolved by alcohol,	7.91
Weight of residue,	4.34

IV. 9.3 grams of diazo compound were dissolved in 200 cc. of absolute alcohol.

Weight of barium salts,	11.24 grams.
Weight of portion dissolved by alcohol,	6.88
Weight of residue,	4.26

The averages of the numbers representing the two products stand in the ratio of 7.16 to 4.17, the ethoxy compound constituting 62.2 per cent. of the total. There is greater difference between this number and that obtained in the last series, than between the latter and that preceding it. This fact is suggestive. The same tendency will be noticed in the next series.

Experiments at 800 *mm. Pressure.*—I. 10 grams of diazo compound were decomposed in 200 cc. of absolute alcohol. There was little, if any, odor of aldehyde perceptible. The decomposition was more rapid than in any previous experiment with strong alcohol, being complete in five minutes. The solution after decomposition was colored a pale yellow. Indeed it appears that the higher the pressure at which the decomposition is made, the cleaner is the reaction. The barium salts were entirely free from color.

Weight of barium salts,	12.07 grams.
[A] Weight of portion dissolved by alcohol,	8.60
[B] Weight of residue,	3.30

Analysis of [A].—0.2319 gram of anhydrous salt gave 0.0963 gram of barium sulphate.

	Calculated for $C_6H_3\begin{cases}CH_3\\SO_3\\O.C_2H_5\end{cases}Ba$	Found.
Ba	24.16	24.37

Analysis of [B].—0.2102 gram of anhydrous salt gave 0.1017 gram of barium sulphate.

	Calculated for $C_6H_3<^{CH_3}_{SO_3}ba$	Found.
Ba	28.60	28.40

II. 9.6 grams of diazo compound were decomposed in 200 cc. of absolute alcohol. The same phenomena were noted as before.

Weight of barium salts,	12.01 grams.
Weight of portion dissolved by alcohol,	8.19
Weight of residue,	3.79

III. 9.6 grams of diazo compound were decomposed in 200 cc. of absolute alcohol.

Weight of barium salts,	11.7 grams.
Weight of portion dissolved by alcohol,	8.02
Weight of residue,	3.57

The averages, taken as in former cases, stand in the ratio of 8.24 to 3.55, the ethoxy compound representing 69.8 per cent. of the total.

The experiments at 800 mm. pressure conclude the decompositions made by us. It will be noticed that in each series there are small differences in the relative quantities of the two products obtained. These discrepancies may be due to actual lack of constancy in the course of the reactions, but are more probably owing to imperfections in the method of work. There is evidently a marked tendency in the results that is unmistakable. It was suggested by Remsen and Palmer that increased pressure favors the ethoxy reaction. The results here recorded confirm this conclusion. Summarising these results at the various pressures, we find a remarkable degree of regularity in the increase of the proportion of ethoxy product with increase of pressure.

Pressure.	Ethoxy Product.
120 mm.	37.2 per cent.
210	40.6
300	43.4
400	48.7
500	52.8
600	57.7
700	63.2
800	69.8

With one exception, the differences between the percentages of ethoxy product for proximate experiments increase slightly as the pressure is increased. A curve representing the course of the reaction as influenced by pressure is given on the accompanying page. It approximates very nearly to a parabola, the point lying farthest from the curve being out of position only one per cent.

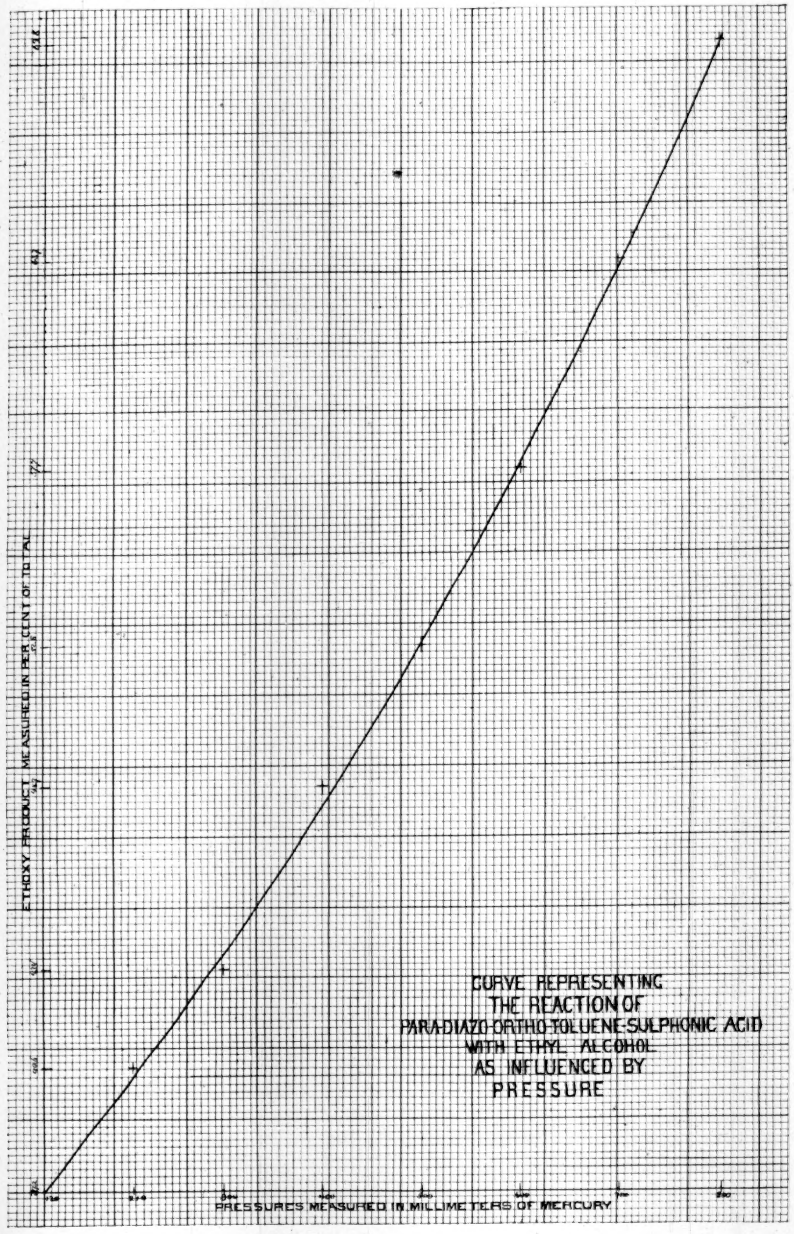
III.—Influence of Temperature in the Decomposition of the Diazo Compound.

A question will naturally suggest itself as regards the temperature at which the decompositions were effected. Boiling under increased pressure requires, of course, a higher temperature than boiling at lower pressure. It was noticed that the decomposition usually began immediately upon boiling, but constant boiling was not necessary for its continuance. Experiments were made with a view to ascertaining the temperature of the alcohol during decomposition under the various conditions of pressure. The following results were obtained in several series of observations:

Pressure.	Temperature.
120 mm.	84°
210	87
300	90
400	92½
500	94½
600	97
700	99
800	102

The network of wire and the curvature of the sides of the flask rendered close reading impossible. As far as could be observed, the temperature during decomposition at any given pressure remained constant.

The question whether the difference in the course of the reactions involved in the decomposition at different pressures is due directly to change in pressure or to change of temperature caused by change of pressure, cannot be answered definitely by the aid of the experiments described above. In all of them the desired pressure was obtained by heating the flask rapidly, until the alcohol vapors and nitrogen given off in decomposition produced



CURVE REPRESENTING
THE REACTION OF
PARA-DIAZO-ORTHO-TOLUENE-SULPHONIC ACID
WITH ETHYL ALCOHOL
AS INFLUENCED BY
PRESSURE

the desired effect. To decide the question at issue, the following experiments were tried: The decomposition flask was connected through suitable drying apparatus with a second balloon flask containing a strong solution of ammonium nitrite. By warming this nearly to the boiling-point, nitrogen was given off freely. The pressure was regulated by the valve connected with the flask, and was measured in the usual way by the manometer in connection with the decomposition flask. It was thus found possible to produce any desired pressure without introducing any substance not already present in the products of decomposition, and maintain it very constantly quite independently of the temperature of the contents of the decomposition flask. The desired pressure being established, the flask was heated to any desired temperature. It was found that at low temperature and high pressure the diazo compound was not decomposed. On raising the temperature gradually, decomposition began when it approached the boiling-point of alcohol under the pressure maintained in the experiment. On the other hand, keeping the lower temperature, and lowering the pressure, little decomposition was noticed until like conditions as to temperature and pressure were produced. In other words, it appears that for decomposition at any given pressure, a definite temperature is necessary, and this temperature lies very near the point at which the alcohol boils at that pressure. The temperature being kept constant, if the pressure be increased, decomposition is interfered with. The reason for this is unknown.

The decomposition of the diazo compound appears to be influenced by temperature as well as by pressure. To which should be ascribed the cause of the regular differences noted in the experiments under the various conditions, it is impossible at present to say.

PARAETHOXYORTHOTOLUENESULPHONIC ACID AND SOME OF ITS DERIVATIVES.

By Paul J. Dashiell.

In the course of the investigation the results of which are described in the preceding article, a considerable quantity of the barium salt of paraethoxyorthotoluenesulphonic acid was collected, and as but few of its derivatives had been previously made, I prepared and studied some of these. The amide made in the usual way was found to melt at 143°–144°, as stated by Remsen and Palmer.[1]

Paraethoxyorthotoluenesulphonic Acid, $C_6H_3\begin{cases}CH_3\\SO_3H(o)\\O.C_2H_5(p)\end{cases}$. — Made from the purified barium salt (description given below) by precipitating the metal exactly with dilute sulphuric acid—forms a brownish yellow, crystalline, hygroscopic mass, difficult to dry. No analysis was made. The acid was used in the preparation of various salts.

Barium Salt, $\left(C_6H_3\begin{cases}CH_3\\SO_3\\O.C_2H_5\end{cases}\right)_2 Ba.4H_2O$. — Prepared by repeated recrystallisation from alcohol and water of the crude product obtained from the decompositions; forms white, shining leaflets, apparently of the monoclinic system; fairly soluble in cold water, readily in hot water; difficultly soluble in cold alcohol, more readily in hot alcohol.

0.2531 gram of salt lost at 150° C. 0.0282 gram of water and gave 0.0922 gram of barium sulphate.

0.2539 gram of salt lost 0.0287 gram of water and gave 0.0920 gram of barium sulphate.

	Calculated for $\left(C_6H_3\begin{cases}CH_3\\SO_3\\O.C_2H_5\end{cases}\right)_2 Ba.4H_2O$.	Found.
H_2O	11.26	11.14–11.30
Ba	21.44	21.42–21.38

Lead Salt, $\left(C_6H_3\begin{cases}CH_3\\SO_3\\O.C_2H_5\end{cases}\right)_2 Pb.3H_2O$. — Prepared by neutralisation of the acid with excess of pure lead carbonate; forms

[1] This Journal **8**, 243.

colorless, well-formed, lustrous leaflets, arranged in radial clusters; sparingly soluble in cold water and in alcohol, very soluble in both when hot.

0.2223 gram of salt lost at 130° C. 0.0177 gram of water and gave 0.0969 gram of lead sulphate.

0.1995 gram of salt lost 0.0158 gram of water and gave 0.0863 gram of lead sulphate.

	Calculated for $\left(C_6H_3\begin{cases}CH_3\\SO_3\\O.C_2H_5\end{cases}\right)_2Pb.3H_2O$.	Found.
H_2O	7.82	7.96– 7.91
Pb	29.85	29.72–29.50

Calcium Salt, $\left(C_6H_3\begin{cases}CH_3\\SO_3\\O.C_2H_5\end{cases}\right)_2Ca.3H_2O$.—Prepared by neutralisation of the free acid with finely divided calcite; forms lustrous, prismatic crystals, showing tendency to penetration twinning; exceedingly soluble in water, fairly soluble in alcohol.

0.2524 gram of salt lost at 230° C. 0.0266 gram of water and gave 0.0660 gram of calcium sulphate.

0.2421 gram of salt lost 0.0250 gram of water and gave 0.0633 gram of calcium sulphate.

	Calculated for $\left(C_6H_3\begin{cases}CH_3\\SO_3\\O.C_2H_5\end{cases}\right)_2Ca.3H_2O$.	Found.
H_2O	10.30	10.53–10.32
Ca	7.63	7.64– 7.43

Magnesium Salt, $\left(C_6H_3\begin{cases}CH_3\\SO_3\\O.C_2H_5\end{cases}\right)_2Mg.5H_2O$.—Prepared by neutralisation of the acid with pure magnesium carbonate; crystallises in long, narrow plates, more than an inch long, closely matted together and showing transverse striations, apparently due to twinning; fairly soluble in water, less so in alcohol.

0.2037 gram of salt lost at 135° C. 0.0338 gram of water and gave 0.0465 gram of magnesium sulphate.

0.2243 gram of salt lost 0.0374 gram of water and gave 0.0478 gram of magnesium sulphate.

	Calculated for $\left(C_6H_3\begin{cases}CH_3\\SO_3\\O.C_2H_5\end{cases}\right)_2Mg.5H_2O$.	Found.
H_2O	16.53	16.59–16.32
Mg	4.48	4.56– 4.30

Zinc Salt, $\left(C_6H_3\begin{matrix}\diagup CH_3\\ —SO\\ \diagdown O.C_2H_5\end{matrix}\right)_2 Zn.6H_2O$.—Prepared by neutralisation of the acid with pure zinc carbonate; crystallises remarkably well in thick, colorless, transparent, striated plates; easily soluble in water and alcohol.

0.2291 gram of salt lost at 150° C. 0.0406 gram of water and gave 0.0606 gram of zinc sulphate.

0.2511 gram of salt lost 0.0454 gram of water and gave 0.0666 gram of zinc sulphate.

	Calculated for $\left(C_6H_3\begin{matrix}\diagup CH_3\\ —SO_3\\ \diagdown O.C_2H_5\end{matrix}\right)_2 Zn.6H_2O$.	Found.
H_2O	17.91	17.81–17.84
Zn	10.85	10.71–10.70

Copper Salt, $\left(C_6H_3\begin{matrix}\diagup CH_3\\ —SO_2\\ \diagdown O.C_2H_5\end{matrix}\right)_2 Cu.6H_2O$.—Prepared by saturation of the free acid with pure copper oxide; forms thick, lustrous, pale-green plates, closely massed together and showing transverse striations due to twinning; readily soluble in alcohol and water.

0.2441 gram of salt lost at 150° C. 0.0444 gram of water.

0.2350 gram of salt lost 0.0426 gram of water and gave 0.0307 gram of copper oxide.

0.2311 gram of salt gave 0.0301 gram of copper oxide.

	Calculated for $\left(C_6H_3\begin{matrix}\diagup CH_3\\ —SO_3\\ \diagdown O.C_2H_5\end{matrix}\right)_2 Cu.6H_2O$.	Found.
H_2O	17.97	18.18–18.12
Cu	10.52	10.40–10.38

Silver Salt.—Prepared by neutralisation of the acid with pure silver carbonate; crystallises beautifully in well-formed prisms; easily affected by the light, with deposition of silver oxide. Analyses were unsatisfactory on this account.

Potassium Salt, $C_6H_3\begin{matrix}\diagup CH_3\\ —SO_3K.H_2O\\ \diagdown O.C_2H_5\end{matrix}$.—Prepared by exact precipitation of the metal from the barium salt by a solution of potassium carbonate; very soluble in water, but obtained, after evaporation to a small volume, in white leaflets; difficultly soluble in cold alcohol.

0.2622 gram of salt lost at 180° C. 0.0185 gram of water and gave 0.0872 gram of potassium sulphate.

0.2778 gram of salt lost 0.0190 gram of water and gave 0.0916 gram of potassium sulphate.

Calculated for $C_6H_3\begin{cases}CH_3\\SO_3K.H_2O\\O.C_2H_5\end{cases}$		Found.
H_2O	6.62	6.63- 6.76
K	14.88	14.89–14.77

Sodium Salt.—Prepared by neutralisation of the free acid with pure sodium carbonate; so readily soluble in water that evaporation to dryness was necessary in order to obtain it; less soluble in alcohol.

0.2560 gram of anhydrous salt gave 0.0779 gram of sodium sulphate.

0.2453 gram of anhydrous salt gave 0.0753 gram of sodium sulphate.

Calculated for $C_6H_3\begin{cases}CH_3\\SO_3Na\\O.C_2H_5\end{cases}$		Found.
Na	9.64	9.85–9.94

A little of the carbonate was probably present.

Ammonium Salt.—Prepared by neutralisation of the acid with ammonia, driving off the excess on the water-bath and evaporating to dryness, when the salt was obtained as a crystalline yellowish crust, whose underside showed small, shining, plate-like, colorless crystals. No analyses were made.

Chloride of paraethoxyorthotoluenesulphonic Acid,
$C_6H_3\begin{cases}CH_3\\SO_2Cl(o)\\O.C_2H_5(p)\end{cases}$.—Prepared by treatment of the dried and powdered sodium salt with a small excess of phosphorus pentachloride as described in connection with the amide—appeared as a clear, light-brown, mobile oil, with odor characteristic of acid chlorides. Treatment with benzene and with ether failed to produce change beyond mechanical solution, from which the oil was again obtained on distillation of the solvent.

Contributions from the Chemical Laboratory of Harvard College.

LXXV.—ON CERTAIN DERIVATIVES OF PYROMUCAMIDE.[1]

By Charles E. Saunders.

This investigation was undertaken at the suggestion of Professor H. B. Hill, in the hope of obtaining from pyromucamide or its derivatives, through Hoffmann's[2] reaction, an amine having the nitrogen atom directly united to a carbon atom of the furfuran ring, no such amine being at present known. Since preliminary experiments with pyromucamide had shown that the reaction was complicated by products formed through the action of the bromine upon the furfuran group, $\beta\delta$-dibrompyromucamide was chosen as better adapted to the purpose, since the corresponding acid is unaffected by bromine. In this case, however, the product proved to be the nitrile of the acid, instead of the amine with one less carbon atom. The behavior of pyromucamide with dry bromine was next studied, and a stable tetrabromide isolated, and at the same time the action of bromine in aqueous solution upon pyromucamide was examined in order to find an explanation of certain striking color reactions which had previously been observed in this laboratory.

The Action of Bromine and Potassium Hydroxide on $\beta\delta$-Dibrompyromucamide.

Bromine alone has no marked action on $\beta\delta$-dibrompyromucamide, the amide dissolving quietly in the bromine. On evaporating, the amide can be recovered unchanged, though the removal of the last portions of bromine at ordinary temperatures occupies considerable time, indicating perhaps the production of an unstable tetrabromide. Nevertheless, all attempts to prove more definitely the formation of such a product failed. When the amide was dissolved in bromine and the solution treated with aqueous potassium hydroxide, a small yield of a substance insoluble in water was obtained. This was filtered off, washed with water, and

[1] Presented by Henry B. Hill at a meeting of the American Academy of Arts and Sciences, held November 9, 1892.

[2] Ber. d. chem. Ges. **14**, 2725; **15**, 407, 752, 762; **17**, 1406, 1923; **18**, 2734.

distilled with steam. The best yield was obtained as follows. One part of the amide was dissolved in 1.8 parts of bromine (about six atoms of bromine to one molecule of amide) in a large beaker. Over this solution was poured a considerable quantity of a cold five per cent. solution of sodium or potassium hydroxide. The contents of the beaker were kept cold, and allowed to stand, the alkaline reaction being maintained by the occasional addition of a small portion of 20 per cent. sodium hydroxide solution. The insoluble product gradually rose to the surface, as the bromine disappeared, and was skimmed off. It was washed with dilute acid, and then distilled with steam. The yield was nearly 13 per cent. of the weight of amide taken. For further purification the substance was crystallised from a very small quantity of alcohol, solution being brought about at 90° to 100° under pressure.

The substance gave the following results on analysis:

I. 0.4259 gram substance gave 0.3745 gram CO_2 and 0.0160 gram H_2O.

II. 0.2044 gram substance gave 0.3082 gram AgBr.

III. 0.2056 gram substance gave 10.3 cc. of moist nitrogen at 15.3° and 757.5 mm. pressure.

	Calculated for C_5HBr_2NO.	Found. I.	II.	III.
C	23.90	23.98	...	...
H	0.40	0.42	...	...
Br	63.75	...	64.17	...
N	5.58	...	...	5.84

The analysis shows that the substance is not the expected amine, but is $\beta\delta$-dibromfurfuronitrile. This conclusion was confirmed by the reactions of the substance, and by its preparation through the dehydration of the amide, using phosphorus pentachloride as the dehydrating agent. The amide was mixed with the calculated quantity of phosphorus pentachloride, and the mixture heated in a distilling flask to about 200°, until hydrochloric acid ceased to be given off. The contents of the flask were then distilled with steam. The yield of dibromfurfuronitrile was 56 per cent. of the calculated amount. The substance as thus obtained was found to be identical in composition and physical properties with that formed by the action of bromine and dilute potassium hydroxide on the dibromamide. A combustion of this product gave the following results:

0.4272 gram substance gave 0.3793 gram CO_2 and 0.0217 gram H_2O.

	Calculated for C_5HBr_2NO.	Found.
C	23.90	24.21
H	0.40	0.56

Properties of βδ-Dibromfurfuronitrile.—It is a colorless solid, possessing a characteristic and rather pleasant odor. It is volatile with steam, scarcely at all soluble in water, readily soluble in ether and in hot alcohol (especially at 100° under pressure). Its melting-point is 88° (uncor.), and its boiling-point 225° (uncor.). It can be sublimed. It crystallises from superheated alcohol in leaflets or plates. On standing for several days in a warm room with concentrated hydrochloric acid, it is converted into βδ-dibrompyromucamide. When it is heated for about an hour in a sealed tube at 100° with concentrated hydrochloric acid, a considerable amount of βδ-dibrompyromucic acid is formed. Prolonged heating causes blackening.

These two reactions were tried with the nitrile prepared in both ways. In alcoholic solution sodium amalgam formed no reduction product. The nitrile was dissolved in dilute alcohol, and treated with two per cent. sodium amalgam, a current of carbon dioxide being passed through until the action was over. The distillate obtained from this was not alkaline, and gave practically no residue when acidified and evaporated. The residue in the flask gave, on evaporation, needles of βδ-dibrompyromucamide.

When the solution of dibromamide in bromine was treated with dilute cold potassium or sodium hydroxide, the only product found, beside the nitrile, was monobrommaleic acid. This was identified by its melting-point and other physical properties, as well as those of its barium salt.

The dehydration of the dibromamide—under the conditions of the experiments related—with formation of the nitrile, is particularly interesting, because Hofmann[1] found that, in preparing amines from amides by the method introduced by him, nitriles were sometimes produced, chiefly when working with the amides of the higher fatty acids; but the nitriles thus formed always contained one carbon atom less than the amide with which he started, and he considers the amine to be an intermediate product in these cases. In the present instance, however, since the nitrile contains the

[1] Ber. d. chem. Ges. **17**, 1406, 1920.

same number of carbon atoms as the amide, this interpretation of the reaction cannot be applied. The author has no explanation to offer. It is worthy of note that the same reaction takes place, whether the alkali used is potassium, sodium, or barium hydroxide.

The Action of Bromine on Pyromucamide.

The tetrabromide of pyromucamide is obtained by dropping small portions of powdered pyromucamide into bromine kept cooled below zero. One should use 3.6 parts of bromine to one part of pyromucamide; that is, about five atoms of bromine to one molecule of pyromucamide. The liquid becomes thick and should be well stirred. After the pyromucamide has all been added, the excess of bromine is allowed to evaporate, and cold alcohol poured over the well cooled residue. On standing, a pale yellow, finely divided solid separated from the dark mass. After the latter has been completety broken up, the product is filtered off and washed with ether. The yield is between 50 and 60 per cent. of the calculated amount. For further purification the substance is dissolved in ethyl acetate or acetone, and the greater part of the solvent distilled off. It is then filtered, and washed again with ether. The substance is thus obtained in minute, colorless, glistening crystals. An analysis gave the following results:

I. 0.3417 gram substance gave 0.1751 gram CO_2 and 0.0410 gram H_2O.

II. 0.1110 gram substance gave 0.1950 gram AgBr.

III. 0.4586 gram substance gave 13.6 cc. of moist nitrogen at 23.5° and 765 mm. pressure.

	Calculated for $C_5H_5NBr_4O_2$.	Found. I.	II.	III.
C	13.92	13.98	...	...
H	1.16	1.33	...	...
Br	74.25	...	74.76	...
N	3.25	...	...	3.36

The substance is therefore the tetrabromide of pyromucamide.

Properties of Pyromucamide Tetrabromide.—It is a crystalline solid without color or odor. Its melting-point is about 121°, as determined in the ordinary way, but it varies with the rapidity of the heating. By long heating the substance will melt, always with evident decomposition, even below 100°. It is insoluble in water, almost insoluble in ether, chloroform, glacial acetic acid, or

alcohol, somewhat more readily soluble in ethyl acetate and acetone. It is decomposed by boiling with water, alcohol, or glacial acetic acid. When it was dissolved in alcohol and treated with zinc dust in the cold, the bromine was abstracted and pyromucamide formed. On boiling with water it is decomposed; hydrobromic acid is formed, but no definite organic compound could be isolated. In order to study the products formed by the action of alkalies, the tetrabromide was added gradually, in small portions, to *cold* concentrated alcoholic sodium hydroxide. After standing in the cold for about an hour, the mixture was allowed to remain for several days in a warm room, the alcohol being renewed when necessary. Ammonia was slowly evolved. The alcohol was then evaporated off, and the solid residue treated with water. Only a very small portion of insoluble matter was left. This was filtered off. On acidifying the filtrate, an acid was precipitated which was purified by converting it into the barium salt and separating the latter by fractional crystallisation into three portions. The acid was then liberated from each portion separately. It appeared to be $\beta\gamma$-dibrompyromucic acid, since each fraction melted at about 192°, the purest at 191.5°. To remove all doubt, this portion was dissolved in absolute alcohol, and converted into the ethyl ester by the action of dry hydrochloric acid. The observed melting-point of the ester, 67.5°, completed the proof as to the nature of the acid, since the $\beta\gamma$-dibrompyromucic acid melts at 191°–192°, and its ethyl ester at 67°–68°.[1] $\beta\delta$-dibrompyromucic acid does not seem to be formed at all in this decomposition of pyromucamide tetrabromide. Even microscopic examination failed to prove its presence, though the crystals are quite characteristic. This is interesting in consideration of the fact observed by Hill and Sanger,[1] that the tetrabromide of pyromucic acid yields, under similar circumstances, a mixture of the two isomeric dibrompyromucic acids ($\beta\gamma$ and $\beta\delta$).

The Action of Bromine Water on Pyromucamide.

Some remarkable color reactions observed by Professor Hill, when studying the action of bromine and potassium hydroxide on pyromucamide, led to the suggestion that interesting results might be obtained in that direction by further work. The author therefore gave a short time to the study of the nature of these color

[1] Proceedings Am. Academy **21**, 155 *et seq.*

reactions, as well as those produced when bromine water is used in place of pure bromine, and when other basic substances are used in place of potassium hydroxide.

Pyromucamide treated with bromine water dissolves readily, producing a solution almost or quite colorless. This was treated in various ways in order to isolate, if possible, some definite substance from it, but amorphous dark products were always obtained. If to the fresh solution there is added almost any strongly basic inorganic substance, a dark blue (or sometimes purple) color is soon produced, the rapidity of its production depending apparently on the strength of the base. The color usually changes to purple in a short time, and afterwards undergoes other alterations, generally passing to red, and finally, if the amount of pyromucamide used is small, fading to pale yellow. When the base employed is barium hydroxide, a dark blue amorphous precipitate is produced. An investigation was made as to the quantity of bromine required to produce the maximum intensity of color from a given amount of pyromucamide. Measured quantities of dilute solutions of pyromucamide and bromine were mixed, shaken, and allowed to stand a few moments. Then an excess of sodium hydroxide was added, and the colors produced were compared. It was found that two atoms of bromine to each molecule of pyromucamide gave the deepest color on subsequent treatment with alkali. Either a deficiency or an excess of bromine is unfavorable to the color production. The dark blue compound was too unstable for isolation.

The production of this color may serve as a very delicate test for pyromucamide. When one milligram of the amide is dissolved in a drop of dilute bromine water, and the solution made alkaline, the blue (or purple) color produced is quite distinct.

Chlorine water can be used instead of bromine water, but the color was not obtained when iodine or nitric acid was employed. Substituted pyromucamides, so far as investigated, do not give the color reaction: δ-methylpyromucamide, $\beta\delta$-dibrompyromucamide, and $\beta\gamma$-dichlorpyromucamide were tried.

If instead of sodium hydroxide, an aqueous solution of aniline is added to the solution of pyromucamide in bromine water, a *reddish precipitate* is produced. This substance is not stable. It melts at about 78°, and appears to undergo decomposition when treated with alcohol even in the cold.

By substituting a saturated aqueous solution of phenylhydrazine

for aniline, a brilliant red precipitate was obtained. The most convenient method for preparing this substance is as follows: Dissolve a weighed amount of pyromucamide in as small a quantity of water as convenient; add to this bromine, a few drops at a time, shaking the flask and keeping it cool, until for each molecule of pyromucamide two atoms of bromine have been added. The bromine will be dissolved, and the solution will be almost colorless. Filter if necessary, and add a large excess of a saturated solution of phenylhydrazine in water. Allow the mixture to stand for some time, filter off the red precipitate formed, wash with water, then with two or three small portions of alcohol, and lastly with ether. Dry over sulphuric acid or in a steam-drying oven. The yield is about 1.6 times the weight of the amide taken. The substance as thus obtained is bright red in color. It has no definite melting-point, but darkens in color between 150° and 160°. It is dissolved, and probably decomposed, by aqueous or alcoholic potassium hydroxide, with a marked increase in the intensity of the red color. It is very slightly soluble in chloroform, ether, and carbon disulphide, somewhat more readily in alcohol and acetone. Boiling with alcohol and other solvents decomposes it, but it can be obtained in small scale-like crystals by making a saturated solution at 50° in alcohol or acetone, and allowing it to cool and evaporate spontaneously. The crystals are darker in color than the amorphous material, and are quite brilliant. Qualitative tests showed the absence of bromine. Analyses of the substance, both in the crystalline and the amorphous state, were made with identical results.

The material used in analyses I and II was crystallised from acetone, washed with ether and dried at 100°, while in analyses III and IV an amorphous preparation was used which had been washed successively with water, alcohol, and ether, and dried over sulphuric acid.

I. 0.3001 gram substance gave 0.6684 gram CO_2 and 0.1423 gram H_2O.

II. 0.1005 gram substance gave 17.2 cc. of moist nitrogen at 23.5° and 754 mm. pressure.

III. 0.1740 gram substance gave 0.3879 gram CO_2 and 0.0857 gram H_2O.

IV. 0 2196 gram substance gave 37.9 cc. moist nitrogen at 21.5° and 741 mm. pressure.

	Calculated for $C_{11}H_{11}N_3O_3$.	Found. Crystalline.		Amorphous.	
		I.	II.	III.	IV.
C	60.83	60.74	...	60.80	...
H	5.07	5.27	...	5.47	...
N	19.35	...	19.08	...	19.10

The formula of the substance $C_{11}H_{11}N_3O_3$ shows that it contains the elements of one molecule of phenylhydrazine, and one of pyromucamide, less two atoms of hydrogen. Lack of time prevented a more extended study of this body, but the investigation will be continued at some future time in this laboratory.

REVIEWS AND REPORTS.

Recent Progress in Physical Chemistry.

The Theory of Solutions.

1. *Non-electrolytic solutions.*—The early development of van't Hoff's Theory of Solutions has been reviewed in this Journal **12**, 130, and it seems now in place to consider in outline the work which has since been done. The principle of van't Hoff's derivation[1] of the laws governing the changes of the vapor-pressures, boiling-points and freezing-points of solutions should first be clearly stated. Since the general equation $pv = RT$, summarising the laws of Boyle, Gay-Lussac and Avogadro, had been shown to be the equation of condition for solutions, it became at once possible to carry through various reversible cycles of operations with solutions, and thereby make application of that eminently fruitful principle, the second law of thermodynamics.

a. The vapor-pressure law.—In a reversible cycle at constant temperature, that amount of solvent containing 1 g-molecule of dissolved substance in dilute solution is removed by means of a cylinder and semi-permeable piston. The work done is pv, or $2T$. Suppose the solution to contain [illegible] molecules substance in N g-molecules solvent. The solvent contained is vaporised at its vapor-pressure f, yielding work [illegible] expanding the vapor to the pressure f' of the solution [illegible] $= (f - f')v$ or

[1] van't Hoff: Zeit. f. ph. Ch. **1**, 481 (1887).

$N/n.2T.(f-f')/f$. Condensing the vapor in contact with the solution work $N/n.2T$ is required. The gain of work $N/n.2T.(f-f')/f$ must then equal the initial expenditure $2T$, giving

$$(f-f')/f=n/N,$$

the vapor-pressure law.

b. The boiling-point law.—Consider the same solution as above. N/n g-molecules of solvent are freed in the same way as before and are vaporised at the absolute boiling temperature T of the solvent, absorbing $N/n.\rho$ cal., ρ representing its molecular heat of vaporisation. Heat solvent and solution to the latter's boiling-point $T+\Delta T$, and condense the vapor in contact with the solution, gaining a greater quantity of heat $N/n.\rho'$ cal. Cool ΔT degrees, completing the cycle. According to the first law of thermodynamics,

$$N/n.(\rho'-\rho)=2T.$$

$\int dQ/T$ becomes for this case $\Sigma Q/T=0$, or

$$\frac{\frac{N}{n}\rho}{T}=\frac{\frac{N}{n}\rho'}{T+\Delta T}, \text{ whence}$$

$$\frac{\Delta T}{n}=\frac{1}{N}\cdot\frac{2T^2}{\rho}, \text{ or } \frac{\Delta T}{n}=\frac{0.02\,T^2}{r}$$

for 100 g. solvent, r representing its specific heat of vaporisation. $\Delta T/n$ is the molecular rise of boiling-point.

c. The freezing-point law.—By means of a reversible cycle of the same nature as the preceding, commencing at the absolute freezing temperature T of the solvent and freezing the solvent gained instead of vaporizing it one obtains, λ representing the molecular heat of fusion of the solvent at T,

$$\frac{N}{n}\left(\lambda-\lambda'\right)=pv=2T,$$

$$\frac{\frac{N}{n}\lambda'}{T-\Delta T}=\frac{\frac{N}{n}\lambda}{T}, \text{ whence}$$

$$\frac{\Delta T}{n}=\frac{1}{N}\cdot\frac{2T^2}{\lambda}, \text{ or } \frac{\Delta T}{n}=\frac{0.02\,T^2}{l}$$

for 100 g. solvent, l representing its specific heat of fusion. $\Delta T/n$ is the molecular depression of the freezing-point.

The direct methods of measuring the pressures exerted by dissolved substances require the elimination of the counterbalancing inner pressure (*Binnendruck*), normal to the surface of the liquid. From the assumptions of the kinetic theory of gases van der

Waals has calculated this inner pressure to have for ether the enormous value of about 1300 atmospheres. The following ingenious calculation of the same quantity is due to Stefan.[1] The work required to bring a small portion of the liquid from the interior to the surface of its volume v, against this inner pressure P, is $(P-p)v$, p representing the vapor-pressure. This portion of liquid is now free from the attraction of half the surrounding mass, an additional equal amount of work frees it from the attraction of all and it becomes vapor. The total work is the heat of vaporation r, *i. e.* $2(P-p)v=r$, or for the actual inner pressure $P-p=r/2v$. For one gram ether at 0° C. $r=86$ cal.$=86\times 42\,355$g-cm., $v=1.37$ ccm., 1 atm.$=1033.2$g/cm^2, so that

$$P-p=\frac{86\times 42\,355}{2\times 1.37\times 1033.2}=1287 \text{ atm.}$$

An interesting and simple deduction has been given by Fick.[2] The total pressure under which a solution stands must be the sum of the partial pressures of dissolved substance and solvent, each being proportional to the concentration, and unit molecular concentration (1g-mol. per liter) causing a pressure of 22.35 atm. Pfeffer found the osmotic pressure of a one-per cent. cane-sugar solution to be 49.3 cm. mercury. In this solution the molecular concentration of the water is 1881 times that of the sugar, and its partial pressure is greater in the same ratio. The solution stands then under a total pressure of

$$\frac{1882\times 49.3\times 13.57}{1033.2}=1219 \text{ atm.},$$

the sp. gr. of mercury being 13.57. This figure is in striking agreement with the results of van der Waals (near 1300) and Stefan (1287).

In a comparison of the osmotic pressures observed in the protoplasma cells of different organisms, Tammann[3] has called attention to the singular fact that these pressures are in most cases equal. In the cells of the nerves of frog's legs, in the red blood corpuscles, in the sea algae, and in the cells of land plants the pressure has a constant value of about 4.5 atmospheres. In the cells of the bacteria the osmotic pressure is great, about 16 atmospheres, corresponding to the fact that their activity is a destructive one, transforming compounds of high molecular weights into such of lower. It is evident how greatly this abnormal capacity for resistance supports them in their destructive work.

Beckmann's boiling-point method of determining molecular weights was reviewed in this Journal **12**, 134; since that time Beckmann's experimental results[4] have appeared. A large number of eminently satisfactory determinations were made in the

[1] Stefan: Wied. Ann. **29**, 655 (1886).
[2] Fick: Zeit. f. ph. Ch. **5**, 526 (1890).
[3] Tammann: Zeit. f. ph. Ch. **8**, 685 (1891).
[4] Beckmann: Zeit. f. ph. Ch. **6**, 437 (1890).

following ten solvents; the molecular rise of boiling-point $\Delta T/u$ and the specific heat of vaporisation being given for each as follows:

	$\Delta T/u$.	r.
Ethylene bromide	63.2	51.8
Chloroform	36.6	61.0
Benzene	26.7	93.4
Ethyl acetate	26.1	92.7
Acetic acid	25.3	121.0
Carbon bisulphide	23.7	84 8
Ethyl ether	21.1	90.1
Acetone	16.7	129.7
Ethyl alcohol	11.5	214.9
Water	5.2	536.4

An example is an experiment with benzophenone in carbon bisulphide:

g. substance.	g. solvent.	ΔT.	mol. wt.	Theory.
1.4699	90.60	0.211	182	182
2.9050	...	0.406	187	...

In this paper Beckmann shows conclusively that the needful constant $\Delta T/n$ is to be directly and accurately determined from the heat of vaporisation of the solvent, according to van't Hoff's formula $\Delta T/n = 0.02\, T^2/r$. The author points out that the different solvents can be arranged in a series with respect to their "dissociating force," water coming first, with its capacity of often effecting dissociation into ions. Acetic acid strikingly, the alcohols, phenols, esters, ethers, and to a certain extent acetone, effect solution of substances with normal molecular weights. A tendency to the formation of double molecules is exhibited by some organic acids, oximes and phenols when dissolved in anethol, azobenzene and paratoluidine, and still more strongly when in the hydrocarbons, ethylene bromide, CS_2, and $CHCl_3$. The new method can yield, however, better practical results than vapor density determinations when, as is usual, the *smallest* mol. wt. is desired, since many solvents have a greater dissociating force than has a vacuum.

Certain improvements in the boiling apparatus, adapting it to high-boiling solvents, are described in a further paper.[1] Beckmann has recently shown[2] how his freezing apparatus may be employed in working with high-melting solvents, and has described a simple arrangement for avoiding the absorption of moisture by hygroscopic solvents, by means of a gentle current of dried air passed into the apparatus. A little moisture may often have a serious effect in changing the freezing-point, owing to the low molecular weight of water.

[1] Beckmann: Zeit. f. ph. Ch. **8**, 223 (1891).

[2] *Ibid.* **7**, 323 (1891).

Successful and extended application of van't Hoff's formula $\Delta T/n = 0.02\, T^2/r$ (or l), in the determination of heats of vaporisation and of fusion by the boiling and freezing-point methods, has been made by Eyckman and by Beckmann. See Zeit. f. ph. Ch. **2**, 964; **3**, 113; **3**, 203; **3**, 603; **4**, 497; **6**, 461.

Van't Hoff's vapor-pressure law of solutions has been applied by Ramsay[1] to a study of the molecular weights of the metals dissolved in mercury as amalgams. The method employed was that of direct measurement of the vapor-pressures in barometer tubes. Li, Na, K, Mg, Mn, Zn, Ga, Cd, Ag, Sn, Sb, Au, Tl, Pb, Bi, were found to have monoatomic molecular weights. The molecular weights found for Ca and Ba were about half the recognised atomic weights, yet the figure for Ca is stated to be very uncertain. Al gave values 33–37.

From freezing-point depressions of amalgams Tammann[2] found monoatomic molecular weights for K, Na, Tl and Zn. Heycock and Neville[3] found normal atom depressions for solutions of Au, Tl, Hg, Cd, K, In, in sodium. In tin the theoretical depression is about 3°, and normal values averaging 2.83 were obtained from Ni, Ag, Au, Cu, Tl, Na, Pd, Mg, Pb and Zn. Cd, Hg, Bi and Ca gave somewhat lower values, In and Al tended apparently to form double molecules. Antimony *raised* the freezing-point, a singular phenomenon whose explanation is given below in the review of van't Hoff's theory of solid solutions.

Nernst has shown[4] that the osmotic pressure of solutions requires an opposed "solution pressure" of the dissolving substances, causing their diffusion into the solvent, and measured by the pressure of the saturated solution. This is in every respect analogous to the "vapor pressure" of a substance, measured by the pressure of its saturated vapor. Both pressures being exactly alike, the quantitative relations derived for the one are derivable for the other, and hence the general thermodynamical vapor-pressure formula $dp/dT = s/T.\Delta v$ represents in exact form the change of pressure of a saturated solution with changing temperature, as dependent upon the heat of solution s (thermodynamically defined as the heat-quantity *added*) and volume-increase Δv. From this equation the interesting conclusion has been drawn by Le Chatelier,[5] and also by van't Hoff,[6] that since T and Δv are essentially positive quantities, dp/dT and s must have the same sign. If the dissolving be accompanied by heat-absorption, the pressure p of the saturated solution, and necessarily also its concentration, increase with rising temperature, the reverse taking place if heat be evolved. The relation is extensively supported by experimental evidence.

[1] Ramsay: Jour. Chem. Soc. 1889, 521.
[2] Tammann: Zeit. f. ph. Ch. **3**, 441 (1889).
[3] Heycock and Neville: Jour. Chem. Soc. 1889, 666; 1890, 376.
[4] Nernst: Zeit. f. ph. Ch. **4**, 150 (1889).
[5] Le Chatelier: Comptes rendus **100**, 441 (1885).
[6] van't Hoff: Archives néerlandaises **20**, 53 (1886).

For the solution of one g-molecule of a substance, Δv in the above equation becomes v, whose value is obtainable from the gas equation $pv = RT$, giving

$$\frac{dp}{dT \cdot p} = \frac{s}{RT^2} \text{ or } \frac{d \log p}{dT} = \frac{s}{RT^2}.$$

van't Hoff has [1] used this equation to calculate the heats of solution of substances from their solubility curves, determining the change in the logarithms of the concentrations ($d\log p$) for a small finite temperature change (dT), and setting for T the average temperature of the experiment. The electrolytic dissociation of the substances considered requires that the gas-constant R be multiplied by the coefficient i, representing the increased total number of g-molecules present per g-formula weight, *i. e.* $pv = iRT$. Solving for s he obtained, for example, such results as:

	Temperatures.		Solubilities.		i.	s/100. Theory.	s/100. Observed.
Lime	15.6	54.4	0.129	0.103	2.59	— 28	— 28
K-bioxalate	0	10	2.2	3.1	1.84	+ 98	+ 96
K-bichromate	0	10	4.6	7.4	2.36	+ 173	+ 170

A third conclusion has been drawn from the equation $dp/dT = s/Tv$, and experimentally verified by J. Walker [2] in Ostwald's laboratory. The vapor-pressure curves of a solid and liquid intersect, at the melting-point, at an angle dependent upon the heat of fusion. The solubility of a substance suffers with increasing temperature no discontinuous change on passing its melting-point, yet the solubility curves of solid and liquid must here intersect at an angle dependent upon the heat of fusion. Integrating the equation $dp/p = s/2T^2 . dT$, and multiplying by T, we have

$$T \log p = -s/2 + (\log p_0 + s/2T_0)\, T, \qquad (1)$$

T_0 and p_0 representing respectively melting-point and pressure in the saturated solution of the dissolved substance. This relation obtaining for the solid, for the liquid the heat of solution is increased by the molecular heat of fusion λ, or

$$T \log p' = -\frac{s+\lambda}{2} + \left(\log p_0 + \frac{s+\lambda}{2T_0}\right) T. \qquad (2)$$

Assuming s to be constant over the temperature-interval considered, eq. (1) becomes the equation of a straight line, the tangent of whose angle with the T-axis is

$$\tan \alpha = \log p_0 + s/2T_0 \quad \text{or} \quad s = 2T_0 (\tan \alpha - \log p_0).$$

Likewise from (2),

$$s + \lambda = 2T_0 (\tan \alpha' - \log p_0).$$

Subtracting:

$$\lambda = 2T (\tan \alpha' - \tan \alpha).$$

[1] van't Hoff: Archives néerl. **20**, 55 (1886). [2] Walker: Zeit. f. ph. Ch. **5**, 193 (1890).

Tan α is determined experimentally from the solubility curves, from which then the molecular heat of fusion λ of the dissolved substance is obtained. Walker found thus for *p*-toluidine (dissolved in water) 44.5 cal. per gram, approximating the actual value 39 cal. For water (dissolved in ether) 77 cal. was found as against 80 cal., the actual value. Hereby was discovered that water dissolved in ether has the molecular formula H_4O_2, which is interesting in connection with the observation of Eyckman, from the freezing-point method, that water in *p*-toluidine is also H_4O_2. Dissolved in phenol, however, it has the normal molecular weight 18.

Defining solutions as homogeneous mixtures, non-separable into their components by mechanical means, and whose composition can vary without destroying their homogeneity, van't Hoff has shown[1] that in addition to gaseous and liquid solutions, solid ones have a claim for consideration, thus considerably extending the applicability of the general solution laws. Instances of solid solutions are the alloys, isomorphous mixed crystals and the various kinds of glass. That the dissolved substances in solid solution stand under a definite partial pressure, as in the liquid and gaseous ones, is demonstrated by their tendency to diffuse, as in the diffusion of iron into carbon, or the reverse, at high temperatures; of calcium into iron, of copper into platinum, of zinc into copper, and many more.

In the first case cited (iron and carbon), pressure and concentration were experimentally shown to be proportional (Boyle's law), and for solutions of hydrogen in palladium hydride Pd_2H the absorption is proportional to the pressure of the hydrogen gas (Henry's law). Suitable combination of these results shows the pressures in solid solutions to be the same as those in liquid solutions *or gases*, at the same concentrations and temperatures.

Further, that the formation of solid solutions decreases the vapor-pressure appears *e. g.* from the ready weathering of lead thiosulphate, which is greatly diminished by the addition of a small amount of the isomorphous Ca or Sr salt. In fact, in such cases, the resulting solid solutions may have lower vapor-pressures than has either constituent. In the same way the analogous "solution pressures" of salts, and hence their solubilities, are diminished by the formation of mixed crystals.

Since the freezing-point is given by the intersection of the vapor-pressure curves of liquid and solid, it follows that forming a liquid solution depresses the freezing-point, forming a solid solution raises it, and both processes may take place together. Under van't Hoff's direction van Bijlert[2] has shown that this simple explanation accounts for the observed "abnormal" freezing-point depressions, in each case the crystals separated on freezing being a solid solution and not the pure solvent. Further than this, that

[1] van't Hoff: Zeit. f. ph. Ch. **5**, 322 (1890). [2] van Bijlert: Zeit. f. ph. Ch. **8**, 343 (1891).

antimony dissolved in melted tin *raises* its freezing-point has been shown by him to be due to the formation of a solid solution of antimony in tin, the crystals separated on freezing containing even more antimony than the remaining liquid solution.

A recent paper by Küster[1] contains the results of a study of the dependence of the freezing-point of a mixture of two isomorphous organic substances upon its composition. The melting point was found to be an additive property of the mixture, changing directly in proportion to the change of molecular concentration. Such substances as tri-chlor- and tri-brom-acetamide, and dihydro naphthalene and naphthalene, were thus shown to be isomorphous. That the general law for the freezing-points of solutions does not apply in these cases results from the separation of a solid solution (mixed crystals) on freezing, and not the pure solvent as required by the simple van't Hoff formula.

By a most simple application of the Mass Law, from the proportionality between the concentrations of gas and solution, in the case of H_2 dissolved in Pd_2H, van't Hoff has shown this dissolved hydrogen to possess the molecular formula H_2. In a similar way, from Roozeboom's experimental results on the solubilities of mixed crystals, Nernst has calculated[2] the molecular weight of $KClO_3$ in dilute solid solution in $TlClO_3$ to correspond to the molecular formula $KClO_3$ and *not* to $(KClO_3)_2$, double molecules, for example.

TREVOR.

CORNELL UNIVERSITY.

[1] Küster: Zeit. f. ph. Ch. **8**, 577 (1891).

[2] Nernst: Zeit. f. ph. Ch. **9**, 141 (1892).